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Novel approaches for energy efficient solid state lighting by RGB organic light emitting diodes – A review

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ABSTRACT

This paper emphasizes on the novel approaches for energy efficient and eco-friendly solid state lighting. Limitations and global haphazards of currently used lighting systems such as Incandescent lamps, compact fluorescent lamps can be overcome by replacing the present lighting system by green technology called solid state lighting, which is possible only with organic light emitting diodes (OLEDs) and polymer light emitting diodes (PLEDs). This paper also explains important characterization techniques used to evaluate the performance, efficiency, life time; colour rendering index (CRI), Internationale de l'Eclairage (CIE) coordinates and correlated color temperature (CCT) of OLEDs. Review of literature on red, blue, green (RBG) light emitting materials and OLED devices is illustrated since the very first synthesized complex and a range of device architectures are presented and appraised. Measures to increase the efficiency and the life time of OLEDs and handling the degradation issues of the organic materials for OLEDs are also discussed. With these measures if we succeed in improving the efficiency, performance and life time, the present lighting system can be replaced by eco-friendly, energy efficient green technology called Solid state lighting, which would play a significant role in reducing global energy consumption.

Contents

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1. Introduction

Solid state lighting is the alternative lighting achieved by an eco-friendly, energy efficient, new green technology, where illumination is obtained through semiconductor devices like light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs) or light-emitting polymers (LEPs). It has the potential to par exceed the energy efficiencies of incandescent and fluorescent lighting. Cutting-edge research now shows a bright future for solid-state lighting as the next generation of light sources for general illumination, from homes to commercial applications offering low energy consumption and reduced maintenance. Lot of research is going on in developing the eco-friendly materials for emission of light in the required region of visible spectrum and hence this review paper.

2. Back ground of solid state lighting

Lighting technologies are substitutes for sunlight. The history of lighting can be viewed as the development of increasingly efficient technologies for creating visible light in the desired spectral region. The traditional technologies developed so far include incandescence and fluorescence. These technologies have all made significant progress over the past 200 years, but appear to be saturating at efficiencies in the 1–25% range. The newly developed technology called solid-state lighting (SSL), has the potential to reduce lighting energy usage by nearly one half and contribute significantly to our nation's climate change solutions. Novel research is carried out by many researches globally to stimulate the development of the science and technology foundation necessary to enable the promise and potential of solid-state lighting. In practice, there are many challenges at every step of the way and efficiently creating white light from semiconductor materials with band-gaps that span the visible spectrum is extremely challenging. Currently used lighting systems are briefly discussed below.

2.1. Incandescent lamps

Incandescent lamps are generally tungsten filament lamps, which contain vacuum. As filament fracture is the normal end of lamp life it would not be convenient for sub circuits fuses to fail. Tungsten-halogen is a type of incandescent lamp, with tungsten filament just like a regular incandescent lamp; however the bulb is filled with halogen gas. They produce a whiter, more intense light than standard incandescent lamps and are typically used for decorative, display purposes. They are about twice as efficient as regular incandescent lamps and last two to four times longer than most incandescent lamps. Incandescent lamps have relatively short lives (1000–2000 h of use). In fact, only about 15% of the energy they use comes out as light and the rest is released in the form of heat. Incandescent lamps are the least expensive to buy but the most expensive to operate.

2.2. Fluorescent lamps

Fluorescent lamps have emerged as a potent alternative of incandescent bulb because of low power consumption and poor life time. The fluorescent tube has a low pressure of mercury vapor and emits a small amount of blue/green radiation, but the majority is in

Table 1
Efficiency and life time of various lighting technologies.

Technology	Life time (h)	Efficiency (lumen/W)
Incandescent lamp	750–1500	12–18
Halogen lamp	2000–4000	16–29
Linear fluorescent lamp	20,000	80–100
Compact fluorescent lamp	6000–10,000	60–70
White OLEDs	10000	64

the UV at 253.7 nm and 185 nm. The inner wall of the glass has a thin phosphor coating, selected to absorb the UV radiation and transmit it in the visible region. This process is approximately 50% efficient. Fluorescent lamps are about 3–5 times as efficient as standard incandescent lamps and can last about 10 to 20 times longer. Compact fluorescent lamps (CFLs) use gases and phosphor inside the lamp to create light, they are available in screw-in or pin-based configurations, in many sizes and shapes with life time around 7–10,000 h of use. They convert 6.6–8.8% of input power to light, consumes 2–5 times less power, lasts 8–10 times longer compared to an incandescent bulb. CFL exhibits operation optimum performance at 20 °C and its efficiency decreases at higher and lower temperatures.

2.3. LED

LED lamps emit visible light in a very narrow spectral band; they can also generate white light. This is accomplished with either a red–blue–green array or a phosphor-coated blue LED lamp. LED lamps last from 40,000 to 100,000 h depending on the color. LED lamps have made their way into numerous lighting applications including traffic signals, exit signs, under-cabinet lights, and various decorative applications.

2.4. OLEDs: the future of light

Organic light-emitting diodes (OLEDs) are regarded as powerful candidates because they are area lighting sources, which can be driven at voltages as low as just several volts, further, they do not contain mercury, which is harmful to the human body or the environment. As a lighting source for illumination or display backlight, a white light is usually required. This can be achieved by the use of plural light emissive materials such as blue, green, and red. OLEDs produce light in much the similar way that ordinary LEDs do, except that the positive and negative charges originate in organic compounds rather than in crystalline semi-conductors. They emit light across the visible, ultraviolet and infrared wavelengths, with very high brightness and have the potential for energy efficient solutions [1–3].

OLEDs can provide revolutionary lamp properties, which include their excellent transparency, color tunability and flexible lighting sources; they also offer much more freedom in designing lighting [4–7]. OLED technology offers several advantages over conventional lighting. First is its slimness, the thickness of the OLED panel for lighting applications reaches just 1 mm. Such a characteristic may allow OLED lighting to be placed directly on ceilings rather than using fixtures that are suspended from them. In addition, OLED's flexibility may allow lighting fixtures to operate effectively when designed for spaces with limited conditions. Efficiency and life time of various lighting technologies are summarized in Table 1.

3. Structure of OLEDs

A single layer OLED consists of an organic layer sandwiched between two electrodes. This organic layer performs three main functions: hole transport, electron transport and emission. In this case the injection of both the carriers should be same otherwise the device will result in low efficiency because the excess of electrons or holes cannot combine.

In 1960, Pope et al. at New York University developed ohmic, dark injecting electrode contacts to organic crystals. Pope's group first observed electroluminescence under vacuum on a pure single crystal of anthracene and on anthracene crystals doped with tetracene in 1963 using a small area silver electrode at 400 V [8–10]. The structure of this device is shown in Fig. 1. However, this did not attractive the researchers due to its ultra-high voltage and poor device performance.

Their experiment was refined in 1965, demonstrating that in the absence of an external electric field, the electroluminescence in anthracene crystals was due to recombination of a thermalized electron and hole, and the conducting level of anthracene is higher in energy than the exciton energy level [11].

In a two layer OLED two separate layers are used for electron transportation and hole transportation namely electron transport layer (ETL) and hole transport layer (HTL) respectively [12]. The interface provides an efficient site for the recombination of the injected electron–hole pair and results in electroluminescence. In this case the emitter material is doped in one of the two layers. The two layers are used to overcome the problem of low efficiency in case of single layer OLED. Since light emission of OLEDs is directly related to the current density through the organic electro-luminescent medium, the coupling effect of the thin organic layers increases the charge injection and transport efficiencies. This allows acceptable light emission to be achieved with a low bias voltage.

In 1965, Helfrich et al. developed double injection recombination electroluminescence for the first time in an anthracene single crystal using hole and electron injecting electrodes [13]. In the same year, Dow chemical researchers patented a method of preparing electroluminescent cells using high voltage (500–1500 V) AC-driven (100–3000 Hz) electrically-insulated one millimeter thin layers of a melted phosphor consisting of ground anthracene powder, tetracene, and graphite powder [14]. Device performance was limited by the poor electrical conductivity of organic materials but this was overcome with the discovery and development of highly conductive polymers.

The first double layer diode device was reported at Eastman Kodak by Ching W. Tang and Steven Van Slyke in 1987. This device used a novel two-layer structure with separate hole transporting and electron transporting layers such that recombination and light emission occurs in the middle of the organic layer. This resulted in the reduction of operating voltage and improvement in efficiency and led to the era of OLED research and device production. Luminance exceeds 1000 cd/m^2 below 10 V with a quantum efficiency of 1% photon/electron was achieved [15]. Fig. 2 shows

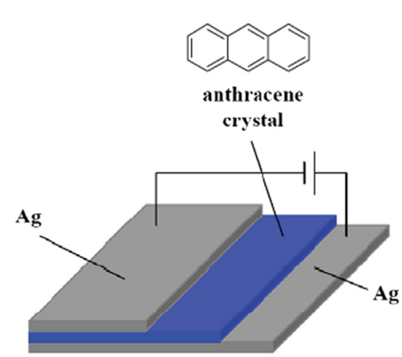


Fig. 1. The structure of the first single layer OLED. Reproduced from Ref. [9].

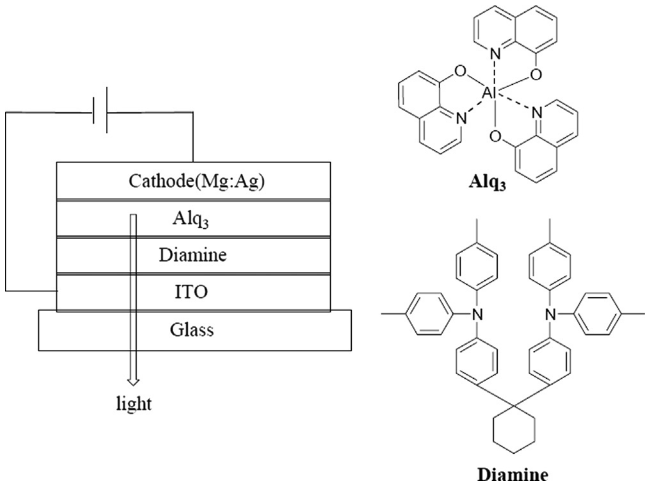


Fig. 2. First double-layer OLED configuration. Reproduced from Ref. [15].

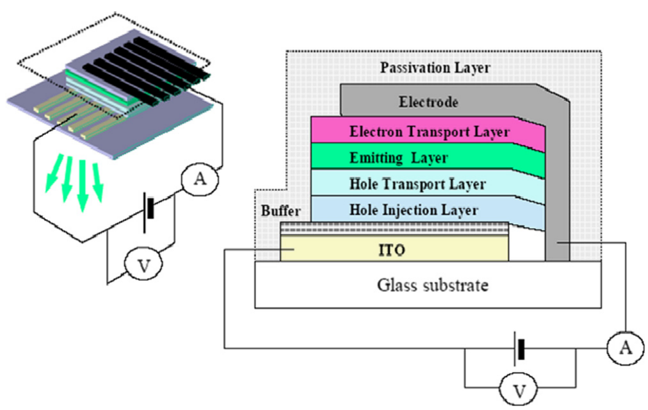


Fig. 3. General structure of multi layer OLED devices.

the first double-layer organic light emitting diode and the structure of the Alq_3 and Diamine organic materials.

In the structure of triple-layer OLED an additional luminescent layer is inserted between the hole and electron-transport layers [16]. This extra layer provides the sites for hole–electron recombination and thus electroluminescence. In this structure, the functions of the individual organic layers are distinct and can therefore be optimized independently. Hence, the luminescence or recombination layer can be chosen to the desired emission color with high luminescence efficiency. Similarly, electron and hole transport layers can also be optimized primarily for the carrier transport property.

In multi-layer OLED, one more layer namely hole injection layer is included. They consists of different layers namely ITO glass plate, hole injection layer (HIL), hole transport layer (HTL), emitting layer (EML), electron transport layer (ETL) and anode. The materials to be used for different layers for OLEDs should meet the requirements like high luminescence efficiency, narrow spectra and correct CIE coordinates, adequate conductivity, good temperature stability, good oxidative stability (water, oxygen) and good radical cation/anion stability, also they should not degrade during sublimation.

In 1995, Sano et al. [17] fabricated multi-layer EL cell with the emission of an Eu-complex formed by vacuum-vapor deposition technique. They used 1AZM-HEX (host material) as a emitting layer and $Eu(TTA)_3Phen$ as a dopant. A red emission at 614 nm with very sharp spectral band was observed from the EL cell with 5 wt% of Eu $(TTA)_3Phen$ and maximum luminance of 137 cd/m^2 was achieved. General structure of multi layer OLED is sketched in Fig. 3.

Materials used for different layers of OLEDs are discussed in detail as follows.

3.1. Substrate materials

Substrate is an essential component of the device or display. The substrate requirements include high transparency, low roughness high surface finish, high flatness, dimensionally stable at processing temperatures and possess high resistance against HNO_3, HF, NaOH [18]. Generally glass is used as substrate as it is rigid and possesses high glass-transition-temperature. Plastic sheets such as clear plastic, metal foil, which is transparent, can also be used as substrate.

3.2. Anode materials

Anode of an OLED must be transparent in order to inject holes into organic layers and highly conductive in order to achieve a device with high performance and efficiency. Indium tin oxide (ITO) is the most widely used anode material with low roughness and high work function (Φ_W=4.5 to 5.1 eV), which is high enough to inject holes into the highest occupied molecular orbital (HOMO) of the organic materials. They should also have good electrical conductivity, high transparency (90%) to visible light and excellent adhesion to the substrates. The conductivity, transparency and work function can all be varied by deposition technique, surface treatment, which includes the use of ozone to interact with the surface in order to increase the work function [19–23].

Recently in 2012, extremely efficient flexible OLEDs with modified graphene anode were fabricated by Han. They achieved extremely high luminous efficiencies (37.2 lm/W in fluorescent OLEDs, 102.7 lm/W in phosphorescent OLEDs), which are significantly higher than those of optimized devices with an indium tin oxide anode (24.1 lm/W in fluorescent OLEDs, 85.6 lm/W in phosphorescent OLEDs) [24]. These results demonstrate the great potential of graphene anodes for use in a wide variety of high-performance flexible organic optoelectronics.

3.3. Hole injection layer (HIL)

This layer injects holes from anode (ITO) to the emissive layer. The materials with high mobility, electron blocking capacity and high glass transition temperature can be used as HIL 4,4′,4tris (3-methylphenylphenylamino)triphenylamine (m-MTDATA) and copper phthalocyanine (CuPc) are the examples of materials used for hole injection layer.

3.4. Hole transport layer (HTL)

Materials having low ionization potential together with low electron affinities and high hole mobility usually function as hole transporting materials by accepting and transporting hole carriers with a positive charge. The most common hole transport materials are N, N′-diphenyl-N, N′-bis(3-methylphenyl) 1,1′-biphenyl-4, 4′ diamine (TPD), N, N′-diphenyl-N, N′-bis(1-naphthylphenyl)-1, 1′-biphenyl-4,4′-diamine (NPB) and 1,10-bis(di-4-tolylaminophenyl) cyclohexane (TAPC). Ongoing efforts on the development of HTLs include the improvement of thermal and electrochemical stability, mobility, glass transition temperature (T_g) and reduction in the energy barrier interface between the anode and ETL and the crystallization behavior.

3.5. Electron transport layer (ETL)

Materials having good electron transporting and hole blocking properties, high electron affinities together with high ionization potentials usually function as electron transporting materials by accepting negative charges and allowing them to move through the molecules. This layer provides an electron conductive pathway for

negative charge carriers to migrate from the cathode into the emission layer. It also prevents the charge leakage and the accumulation of charges at the cathode and ETL interface. The most common ETL materials are Aluminum tris-8-hydroxyquinoline (Alq_3) and 9, 10-di (2-napthyl) anthracene (ADN).

3.6. Emissive layer (EML)

The layer in between HTL and ETL is a good emitter of visible photons, generally known as emissive layer (EML). This layer can be a material made of organic molecules or polymers or dendrimers with high efficiency, lifetime and colour purity. The EML material should have a high glass-transition temperature to obtain devices with longer lifetime.

Depending on the colour required, we can select materials such that the energy gap i.e., the distance between highly occupied molecular orbit (HOMO) and lower unoccupied molecular orbit (LUMO) lies such that the energy released during recombination will be within the desired wavelength.

In OLEDs the emissive layer consists of host and dopants. Host materials transport charge, allow excitons to form and facilitate radiative recombination. The dopants are dispersed in the host layer by using co-evaporation. Emissive materials namely, 4,4,N,N′ dicarbazolebiphenyl(CBP) and1,3-bis(9-carbozoyl)benzene (mCP) are recently developed.

3.7. Cathode materials

The role of cathode is to inject electrons into emitting layers. It must with stand to the organic layers under it. The work function of cathode material should be relatively small ($\varphi_w \approx 2.9$–4.0 eV) so as to minimize the barrier of electron injection. Metals such as lithium, calcium, and magnesium have low work function but they are not used because of their reactive nature. Alloy of magnesium with silver (Mg–Ag) [25] having work function in the range of 3.7 eV and aluminum with alkali metal compounds are generally used as cathode. Aluminum (Al) layer is widely used as the cathode and many other insulating layers such as MgO [26], CsF [27], Al_2O_3 [28] and NaCl [29] have been studied in order to enhance electron injection. For LiF/Al [30,31] cathode, the electron injection enhancement can be explained by tunneling effect at the metal/organic interface, the formation of interfacial dipoles or chemical dissociation of the LiF layer during Al evaporation.

Deposition of all these layers on ITO glass substrate itself is too critical because of the sensitivity of the material to different factors such as high temperature, incorporation of dust during fabrication.

4. Principle and working of OLEDs

Organic light emitting diodes operate on the principle of electroluminescence. The key to the operation of an OLED is an organic luminophore. A great challenge in OLED fabrication is tuning the device such that it allows equal number of holes and electrons to meet in the emissive layer. In an organic compound, this equal balance is very difficult because the mobility of an electron is much lower than that of a hole. When voltage is applied across an OLED; electrical current flows from cathode to anode through organic layers. Cathode gives electrons to the emissive layer of organic molecules, while anode removes electrons from the conductive layer of organic molecules. When the charges in exciton pairs are combined, they give rise to light emission and the color of the light depends on the type of organic molecule in the emissive layer. Light emitting mechanism from an OLED device is shown in Fig. 4. The intensity or brightness of the light depends on the amount of electrical current applied [32].

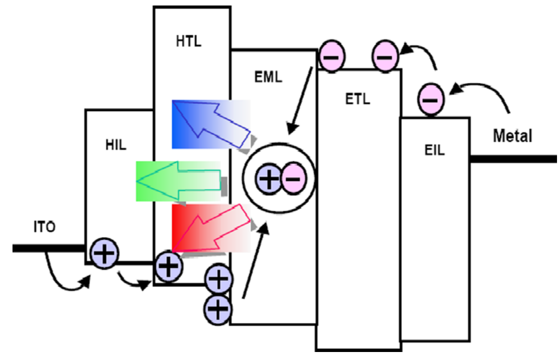


Fig. 4. Working principle of OLED. Reproduced from Ref. [32].

5. Materials for emissive layer of OLEDs

Materials for emissive layer of OLEDs can be broadly classified as small (organic) molecules, polymers and dendrimers. Organic material based electroluminescent (EL) devices have excellent properties of low driving voltage and bright emission [33]. Small molecular organic compounds, conjugated oligomers, polymers with precise chain length, defined electrical and optical qualities are used as organic light emitting materials. Carrier mobility of organic materials is a very important factor for the understanding of operation mechanism in the organic EL devices. As far as conducting polymers are concerned, they must have good solubility, good mechanical properties, high resistance to acids and bases and high conductivity. Dendrimers are the newest class of materials for use in OLEDs.

5.1. Small molecules

They are semi crystalline or crystalline materials with high aqueous solubility. Efficient OLEDs using small molecules were first developed by Tang et al. The first observations of electro luminescence in organic materials were in the early 1950s by Bernanose et al. [34–37].

5.2. Polymers

The light emission colour of the polymers strongly depends on the type of the polymer, its chemical composition and the nature of side groups. Hence, by chemical modification of the polymer structure, a range of soluble light-emitting polymers emitting in the entire VIS spectrum ranging from 400 nm to 800 nm can be made available. The use of emissive additives, also known as dyes is an interesting aspect, which influence the emission colour of light-emitting polymers. By adding a small amount of a suitable dye to a polymer, energy can be transferred from the polymer to the dye there by emission of light from the dye. The colour from the device can be tuned using different dyes. For example, a green dye in a blue polymer will give green light, while a red dye in a blue polymer will give red light. The glass transition temperature T_g, of the polymer materials plays a vital role while selecting the material for the device. The study of the variety of organic materials as active components is determined by the necessity to optimize the characteristics of the devices. Research into polymer electroluminescence culminated in 1990 when Burroughes et al. reported a high efficiency green light-emitting polymer based device using poly(p-phenylene vinylene) [38]. Electroluminescence from polymer films was first observed by Roger Partridge. This device consisted of a film of poly (n-vinylcarbazole) up to 2.2 μm thick located between two charge injecting electrodes [39–43].

Table 2
Properties of small molecules, dendrimers and linear polymers.

S. no.	Property	Small molecules	Dendrimers	Linear polymers
1	**Structure**	Compact	Compact, globular	Not compact
2	**Synthesis**	Solution technique	Careful and stepwise growth	Single step poly condensation
3	**Structural control**	High	Very high	Low
4	**Architecture**	Regular	Regular	Irregular
5	**Shape**	Fixed	Spherical	Random coil
6	**Crystallanity**	Semi crystalline or crystalline	Non-crystalline, amorphous materials	Semi crystalline/crystalline materials
7	**Glass transition temperature**	–	Low	High
8	**Aqueous solubility**	High	High	Low
9	**Nonpolar solubility**	High	High	Low
10	**Viscosity**	Linear relation with molecular weight	Non linear relationship with molecular weight	Linear relation with molecular weight
11	**Reactivity**	Moderate	High	Low
12	**Compressibility**	–	Low	High
13	**Polydispersity**	Monodisperse	Monodisperse	Polydisperse

5.3. Dendrimers

Light emitting dendrimers generally consist of a light-emitting core, to which one or more branched dendrons are attached. Surface groups are attached to the distal end of the dendrons to provide the solubility, which is necessary for solution processing. The dendritic structure allows independent modification of the core (light emission), branching groups (charge transport) and surface groups (processing properties). Properties of small molecules, dendrimers and linear polymers are tabulated in Table 2.

6. Efficiency of OLEDs

The efficiency of an OLED is a function of several factors like efficiency to which the excited state emits light, voltage at which it operates, efficiency of recombination, number of photons emitted to the number of photons absorbed and the degree of balance of charge carrier injection etc. Device performance can be improved by employing highly purified organic complexes, implementing the method of co-doping (a method of co-depositing an appropriate host into organic emitting material), controlling the thickness of each layer, proper selection of HIL, HTL, ETL as well as the device structure.

6.1. Light extraction efficiency in OLEDs

Most of the light generated by an OLED is trapped inside the glass or plastic substrate and wave guided out to the sides; this is normally about 80% of the total. Current research activity is directed towards various surface treatments, which can greatly increase the extraction efficiency.

6.2. Power efficiency in OLEDs

Power efficiency is one of the quantities, which determines how long the battery lasts in a portable device. Power efficiency is measured in lumens per watt. Power efficiency is not only affected by quantum efficiency of the device but also by the voltage at which the device operates. Hence it is important to obtain low operating voltages around 3–6 V, which is related to the charge injection barrier. This avoids expensive voltage up converters to provide compatibility with batteries.

6.3. Recombination efficiency

Recombination efficiency is usually at or near unity; i.e., if two charges come into Vander Wall proximity of each other, then they are guaranteed to annihilate. However, if the annihilation process has no energetic barriers, then quantum spin statistics state that only 25% of the resulting excited states will be useful emissive ones if the state has singlet multiplicity. Although the emission from triplet state is spin forbidden in organic molecules, progress has been made recently in developing triplet state emitters containing at least one atom of higher atomic weight. Even if it is spin allowed, the excited state may still decay non radioactively.

6.4. Luminescence quantum yield

The luminescence quantum yield Φ is also an important parameter for evaluation of efficiency in the emission process involved in luminescent materials. The quantum yield is defined as the ratio of the number of emitted photons to the number of absorbed photons per unit time. Less the number of photons absorbed, more will be the number of photons emitted and hence the luminescence quantum yield.

$$\phi = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}}$$

6.5. Various techniques to improve the efficiency of OLED devices

1. Efficiency of OLEDs is limited because only singlet states are responsible for light emission in undoped devices. The recent developments in harvesting the triplet states, using phosphorescent materials led to an increase in the efficiency and selectivity of possible colors. Electro phosphorescence achieved by doping an organo metallic phosphor into a host has been successfully used for generating the primary colors necessary for display applications [44–46].
2. The doping of the emissive layer in an OLED has been used extensively as a way of improving efficiency, lifetime as well as to modify the emission color. Tang et al. in 1989 first introduced fluorescent dyes, 3-(2-benzothiazolyl)-7-diethylaminocoumarin (coumarin 540) and DCMs as dopants in Alq_3 to improve the efficiency and color purity of the devices [25].
3. The poor light extraction is one of the most important factors, which limits the external quantum efficiency of devices and hence better out coupling methods are to be developed to get higher efficiencies. According to the ray optics, almost about 80% of the light generated from the OLED is lost in wave guided modes due to glass substrate and ITO/organic material i.e, the majority of generated light is either trapped inside the glass substrate and device, or emitted out from the edges of an OLED [47–49]. To extract the trapped and wave guided light into external modes, various approaches based on light refraction and scattering to reduce TIR at the interfaces have been reported, like the use of a shaped substrate [50], use of micro-lenses on

the backside of substrate surface [51,52], formation of monolayer of silica micro-spheres as scattering medium [53,54] and the use of high refractive index substrate [55]. The other approach is to insert an extremely low refractive index silica aerogel layer [56] between the ITO transparent electrode and glass substrate. 50% light extraction efficiency from OLEDs was recently reported by insertion of a two dimensional photonic crystal structure [57].

4. An endothermic energy transfer from a molecular organic host (donor) to an organometallic phosphor (trap) can lead to highly efficient electroluminescence. By u this unique triplet energy transfer process, Do et al. achieved maximum device external quantum efficiency and luminous power efficiency with peak wavelength of 470 nm [58].

7. Fabrication technologies

OLEDs are fabricated by depositing very thin film of organic materials at temperature less than 100 °C to form bright, vivid power efficient, self-emissive light producing elements with fast response times that can be grown on a variety of large area substrates such as glass, plastic or metal foil. These properties make OLEDs ideally suited to enable high information content flexible displays. OLEDs can be fabricated by different techniques, namely Thermal vacuum evaporation, spin-coating, ink-jet printing etc.

7.1. Thermal vacuum evaporation

This technique is used for depositing various active layers in fabricating small molecular organic light emitting devices (SMOLEDs). Vacuum deposition is limited to vaporizable low molecular weight materials and can only be applied to compounds, which endure thermal stress without decomposition. One of the advantages of this technique is that even complicated multilayer device architecture can be constructed without any serious problems. This technology is relatively expensive and of limited use for large-area devices than other processing techniques and can only be applied for smaller devices with high quality [59].

High flexibility in layer design, enabling distinct charge transport and charge blocking layers to be formed is the main reason for the high efficiencies of the small molecule OLEDs. Vacuum-vapour deposition, a conventional and popular technique for fabricating an organic OLED cell, is laborious and not cost competitive. Hence, solution processing techniques such as spin coating technique and ink jet techniques have gained momentum.

7.2. Spin-coating

This technique is used for deposition of soluble polymers on different layers of desired thickness; they provide ease to fabricate monochrome displays. Conjugated polymers can be applied to a surface either through dip-coating or spin-coating. The thickness of the layers is dependent on the composition of the polymer and the concentration of the polymer solution. The production process is comparatively cheaper than vacuum evaporation; this process also enables large area devices with homogeneity throughout the device/display area [60].

7.3. Ink-jet printing

This technique is used for patterning of pixels, manufacturing full-colour display polymer LEDs. Patterning of pixels can be done through ink-jet printing Multilayer preparation from solution is of crucial importance because previously deposited layers are absolutely resistant against the solvent used for deposition of the subsequent layers. Solution techniques provide a means to calculate the energy gap of the synthesized complex [61], which plays a vital role in designing the architecture of the OLED device to be fabricated.

8. Characterization techniques of OLEDs

The performance of OLED devices can be evaluated by current–voltage (*V–I*) characteristics, current density–voltage–luminance (*J–V–L*) characteristics, electroluminescence (EL) spectra, CIE coordinates, color rendering index (CRI), correlated color temperature (CCT), luminous efficacy, life time measurements etc.

8.1. V–I characteristics

V–I characteristics of an OLED device reveals the turn on voltage of the device. The turn on voltage is defined as the voltage necessary to have a luminance of 1 Cd/m^2. Ideally, this value should be as low as possible, but in many lanthanide-based OLEDs the values are between 5 and 10 V. *V–I* characteristics of an OLED device are usually carried out by increasing the voltage, and noting down the corresponding current at a sweep voltage of 1 V at a time interval of 1000 milli seconds (may vary). Usually, with the increase in voltage the current increases exponentially.

8.2. J–V–L characteristics

J–V–L curve characterizes the properties among the current density (*J*), bias voltage (*V*) and the electro luminescence output (*L*). Current density (*J*) is the ratio of current to the area of the device considered. While carrying out *J–V–L* characteristics, the device is focused to spectro radiometer in order to record current and luminance at particular voltage. Current density as well as luminance increases with the drive voltage.

8.3. Electroluminescence (EL) spectra

An electroluminescence (EL) spectrum is a plot between wavelength on the *x*-axis and intensity along *y*-axis. This spectra shows a peak at characteristic wavelength of the emissive material with the application of voltage. The voltage at which OLED starts emitting light is known as turn on voltage, this differs from OLED to OLED. With further increase in voltage, the intensity of light emission increases.

8.4. CIE coordinates

The color of a light source is typically characterized in terms of Commission International de l'Eclairage (CIE) system as shown in Fig. 5. Any color can be expressed by the chromaticity coordinates x and y on the CIE chromaticity diagram as (x, y). Using this method the composition of any color in terms of three primaries can be described [62,63]. Artificial colours, denoted by X, Y, Z are called tristimulus values. By a piece of mathematic legerdemain, it is necessary that the quantity of two of the reference stimuli to define a color since the three quantities (x, y, z) are made always to sum to 1 [64]. The ratios of X, Y, Z of the light to the sum of the three tristimulus values, are called chromaticity coordinates [65].

8.5. Color rendering index (CRI)

Color rendering index attempts to quantify how different a set of test colors appears when illuminated by the source compared to when the same test colors are illuminated by the standard

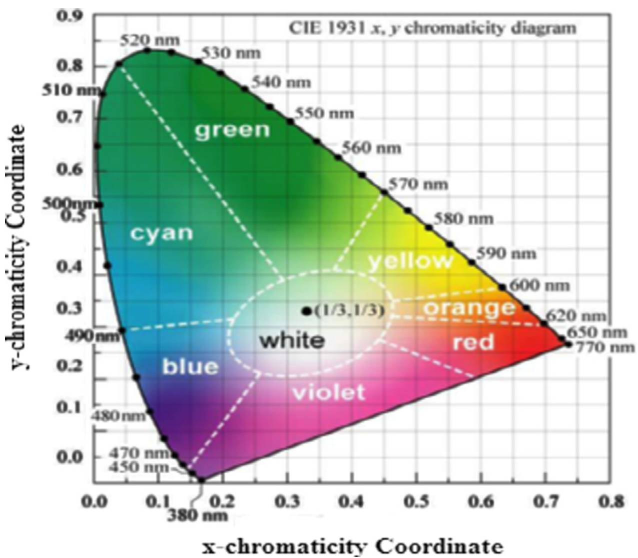


Fig. 5. Chromaticity diagram, representing CIE coordinates of different colours. [65]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

illuminant with the same correlated color temperature. It is measured in 0–100 scale and the highest possible CRI value is 100 and this occurs when there is no difference in color rendering between the light source and the standard illuminant. Color rendering index is a unit less quantity, abbreviated variously as CRI.

8.6. Correlated color temperature (CCT)

Color temperature is the absolute temperature in Kelvin at which a blackbody radiator must be operated to have a chromaticity equal to that of the light source. The light of an incandescent bulb is thermal radiation and the bulb is very close to an ideal black-body radiator, so its color temperature is the temperature of the filament. Color temperature values associated with light sources other than incandescent lamps are correlated color temperature (CCT) and not true color temperatures. For high quality white light illumination the CCT should lie between 2500 K and 6500 K. The CIE, CRI and CCT for common white light sources are given in Table 3 for comparison [66].

8.7. Life time measurements

Luminescence life time of the fabricated device plays a vital role in dictating the performance of the device. For solid state lighting, all the primary colors namely red, blue, green should have good lifetime for their excellent performance. The life of red and green light emitting materials have already reached to their appreciable value, while blue light emitting materials could not accompany with the life time of the other two because the materials usually used for blue light emitting materials have wider band gap which affect their life time, also requires high energy for effective light emission. Luminescence life time is related to the vibration of the nearby ligands used in the synthesized complex. Hence care is to be taken while selecting the ligands during the synthesis of complexes. When these complexes are excited by light energy, the sensitizing ion may absorb light by the vibration of ligand, which may decrease the life time of the complex and hence the device. Commercial viability of OLEDs is hampered by their relatively short usable lifetime, as compared to their inorganic counterparts [67].

Table 3
The CIE, CRI and CCT for common white light sources [66].

Light source	CIE coordinates	CRI	CCT (K)
Incandescent lamp	(0.44, 0.40)	100	2854
Tungsten halogen lamp	(0.44, 0.40)	100	2856
Fluorescent white lamp	(0.37, 0.36)	89	4080
Sodium lamp	(0.51, 0.41)	24	2100
Daylight	(0.31, 0.32)	90	6500
WOLED	(0.33, 0.36)	92	5410

9. Device architectures

9.1. Bottom or top emitting OLEDs

Bottom emission devices use a transparent or semi-transparent bottom electrode to get the light through a transparent substrate, while top emission devices use a transparent or semitransparent top electrode emitting light directly. Top emitting OLEDs are better suited for active matrix applications as they can be more easily integrated with a non-transparent transistor backplane.

9.2. Transparent OLEDs

They use transparent or semi transparent contacts on both sides of the device to create displays. They can greatly improve contrast, making it much easier to view displays in bright sunlight.

9.3. Stacked OLEDs

These OLEDs use a pixel architecture that stacks the red, green, and blue subpixels on top of one another instead of next to one another, leading to substantial increase in gamut and color depth, there by greatly reducing pixel gap. Currently, other display technologies have the RGB pixels mapped next to each other decreasing potential resolution.

9.4. Inverted OLED

In contrast to a conventional OLED, in which the anode is placed on the substrate, an Inverted OLED uses a bottom cathode that can be connected to the drain end of an n-channel TFT especially for the low cost amorphous silicon TFT backplane useful in the manufacturing of active matrix OLED displays [68–70].

10. Review of literature on RGB materials and OLED devices for solid state lighting

White OLEDs offer new design opportunities in practical solid-state lighting and could play a significant role in reducing global energy consumption. Development of new materials for white OLEDs with improved color stability and balanced charge transport properties is a considerable challenge. Major issues involve the fabrication of large area devices and the development of low cost manufacturing technology. White light emission is usually observed by a set of different luminophores with distinct emission colors [71], typically two (blue and orange/yellow) or three (blue, green and red). The most straightforward way to combine different emitters is by blending all of them in a single layer. The first WOLED was fabricated by Kido et al. by doping the hole-conductor poly (N-vinylcarbazole) (PVK) with orange, green and blue emitting dyes in1994 [72]. This review describes the types of materials (small molecules and polymers) that have been used so far to fabricate RBG and hence white OLEDs. A range of device architectures are presented and appraised.

10.1. Red light emitting materials and OLEDs

Rare-earth (RE) β-diketonates play a vital role in red light emitting materials and devices. They are complexes of β-diketones (1,3-diketones) with rare-earth ions. These complexes are most popular and most intensively investigated rare-earth coordination compounds, partially due to the fact that different β-diketones are commercially available and the synthesis of the corresponding rare-earth complexes is relatively easy. However, the main drive for the intense research activity on the rare-earth β-diketonates was and is still continuing because of their potential of being used in several applications.

Rare earths are a family of 17 elements with atomic number 21, 39 and 57 through 71. Out of these, the element with atomic no. 57, lanthanum has no free electron in the 4f shell, while with atomic no. 71; lutetium has a completely filled 4f shell with 14 electrons. One peculiar nature of all 13 elements among the rare earths, starting from Cerium to Ytterbium, is that the 4f shell is incompletely filled, but is completely screened by the outer 5s and 5p sub shells, which are completely filled. The optical and electromagnetic properties of these 13 rare earth elements are essentially due to the screening of this incompletely filled 4f shell. Luminescence in tri positive RE ions arises mainly due to energy level transition within the 4f shell which is generally forbidden by quantum mechanical spin and parity prohibition rules. Efficient luminescence can still occur in these ions under conditions where such ions do not occupy a position having a centre of symmetry in a crystalline lattice. Some of the tri positive ions such as Europium, Terbium and Dysprosium are good luminescent emitters, a factor depending on the number of electrons in its 4f shell. The ions, which are inert to luminescent emission, are those of Yttrium, Lanthanum, Gadolinium and Lutetium. The descriptive classification of rare earths is shown in Table 4 and some of their physical properties of rare earth metals are shown in Table 5.

Lanthanides from Ce^{3+} to Lu^{3+} have one to fourteen 4f electrons added to their inner shell configuration, which is equivalent to Xe. Ion with no 4f electrons i.e. Sc^{3+}, Y^{3+}, La^{3+} and Lu^{3+}, have no electronic energy levels that can induce excitation and luminescence processes in or near the visible region. In contrast, the ions from Ce^{3+} to Yb^{3+}, which have partially filled 4f orbital, have energy levels characteristic of each ion and show a variety of luminescence properties around the visible region. Many of these ions can be used as luminescent ions in phosphors, mostly by replacing Y^{3+}, Gd^{3+}, La^{3+}, and Lu^{3+} in various compounds.

Eu^{3+} ion has a sharp red emission and its complexes are used in OLED's as a red color emitter. Efficient and brighter luminescent complexes can be obtained by (i) selection of proper ligand and (ii) introduction of another metal ion into the complexes. Rare earth complexes exhibit high efficiency along with a narrow emission spectrum [73–76]. It is well established that rare earth metal chelates are characterized by highly efficient intra energy conversion from the ligand singlet (S^1) to the triplet (T^1), and hence to the excited state of the central rare earth metal ion [77,78]. The metal ions exhibit sharp spectral bands corresponding to ^5D_x–^7F_x transitions. This mechanism is characterized by 20–95%

Table 4
Descriptive classification of rare earths.

Light Rare Earth Elements (LREE) **(La to Sa)**	**Common uses**	Heavy Rare Earth Elements (HREE) **(Eu to Lu)**	**Common uses**
Lanthanum-57	Camera lenses, catalytic cracking catalyst for refining oil, high refractive index glass, battery electrodes	Europium-63	Lasers, mercury vapor lamps
Cerium-58	Glass and ceramics, polishing powder, chemical oxidizing agent	Gadolinium-64	Rare earth magnets, lasers, X-ray tubes, MRI, computer memory
Praseodymium-59	Rare earth magnets, lasers, carbon arc lighting	Terbium-65	Lasers, fluorescent lamps
Neodymium-60	Rare earth magnets, lasers	Dysprosium-66	Rare earth magnets, lasers
Promethium-61	Nuclear batteries	Holmium-67	Lasers
Samarium-62	Rare earth magnets, lasers, masers	Erbium-68	Lasers, vanadium steel
		Thulium-69	X-ray machines
		Ytterbium-70	Lasers
		Lutetium-71	PET scanners, high refractive glass

Table 5
Some of the physical properties of rare earth metals.

Element	**Symbol**	**At. no. (Z)**	**Colour**	**Electronic configuration (Ln^{3+})**	**Ground state (Ln^{3+})**	**At. wt. (a.m.u.)**	**Melting point (°C)**	**Boiling point (°C)**	**Density (g/cm³)**	**Crystal structure**
Lanthanum	La	57	White	[Xe]	$^1S_0$	139.91	918	3464	6.145	dhcp
Cerium	Ce	58	White	$[Xe]^4f_1$	$^2f_{5/2}$	140.12	798	3433	6.77	fcc
Praseodymium	Pr	59	Bluish green	$[Xe]^4f_2$	$^3H_4$	140.9	931	3520	6.773	dhcp
Neodymium	Nd	60	Rose violet	$[Xe]^4f_3$	$^4I_{9/2}$	144.24	1021	3074	7.007	dhcp
Promethium	Pm	61	–	$[Xe]^4f_4$	$^5I_4$	147	1042	3000	7.26	dhcp
Samarium	Sm	62	–	$[Xe]^4f_5$	$^6H_{5/2}$	150.35	1074	1794	7.52	rhomb
Europium	Eu	63	Colourless	$[Xe]^4f_6$	$^7F_0$	151.96	822	1529	5.243	bcc
Gadolinium	Gd	64	Colourless	$[Xe]^4f_7$	$^8S_{7/2}$	157.25	1313	3273	7.9	hep
Terbium	Tb	65	Colourless	$[Xe]^4f_8$	$^7F_6$	158.92	1356	3230	8.229	hep
Dysprosium	Dy	66	Shinning Yellow	$[Xe]^4f_9$	$^6H_{15/2}$	162.5	1412	2567	8.55	hep
Holmium	Ho	67	Light yellow	$[Xe]^4f_{10}$	$^5I_8$	164.93	1474	2700	8.755	hep
Erbium	Er	68	Pink	$[Xe]^4f_{11}$	$^4I_{15/2}$	167.26	1529	2868	9.066	hep
Thulium	Tm	69	–	$[Xe]^4f_{12}$	$^3H_6$	168.93	1545	1950	9.321	hep
Ytterbium	Yb	70	–	$[Xe]^4f_{13}$	$^2F_{7/2}$	173.04	819	1196	6.965	fcc
Lutetium	Lu	71	Colourless	$[Xe]^4f_{14}$	$^1S_0$	174.97	1663	3402	9.84	hep

Where hcp, hexagonal close packed; dhcp, double hexagonal close packed; rhomb, rhombohedral; fcc, face centered cubic; bcc, body centered cubic.

photoluminescence efficiency for the molecules suspended in dilute solution [79,80].

Luminescence enhancement of Eu (III) complexes was observed with organic ligand by Yttrium, Lanthanum, Gadolinium and Lutetium and Terbium in Micelle solutions, having the same concentration of each component [81]. Considering these facts and as Y (III), La (III) and Tb (III) predominantly play a role to enhance the luminescence in micelle solution; it has been argued that the efficient and brighter luminescence and economical complexes can be obtained by the introduction of another metal ion into the complex.

The luminescence spectrum of Eu^{3+} in several hosts is composed of groups of several sharp lines. Each group corresponds to transition between an excited and ground state designated by the total angular momentum (*J*). The excitation spectra generally consist of sharp lines due to the 4f→4f transition and of broad bands due to the 4f–5d transition and/or charge transfer process. The lifetimes of the luminescence due to 4f→4f transition are mostly in the range of millisecond because of forbidden character of the luminescence transition. For luminescence due to spin allowed transitions between levels having equal spin multiplicity, a relatively sharp lifetime of $\sim 10^{-5}$ s is observed. Number of lines due to $^5D_j \rightarrow {}^7F_j$ of Eu^{3+} in different host materials are reported. The emission from $^5D_2$ and $^5D_1$ are quenched, with an increase in the Eu^{3+} concentration due to the cross relaxation process, $(^5D_j \rightarrow {}^5D_0) \rightarrow (^7F_0 \rightarrow {}^7F_j)$. The emission in the vicinity of 600 nm is due to the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$, which is insensitive in site symmetry. The emission around 610–630 nm is due to electric dipole transition of $^5D_0 \rightarrow {}^7F_2$, induce by the lack of inversion symmetry at the Eu^{3+} site, and is much stronger than that of the transition to $^7F_1$ state. RE metal complexes have some good characteristics, such as extremely narrow emission line and high internal quantum efficiencies, which are suitable for use as the emission material in OLEDs. They are widely used in cathodoluminescent display phosphor screens, lasers and lamps because; their photoluminescence (PL) exhibits high quantum efficiencies and very sharp spectral line.

In the early 1960s, these compounds were explored as extractants in solvent–solvent extraction processes. In the middle of the 1960s, the rare-earth β-diketonates were recognized as potential active compounds for chelate lasers or liquid lasers. The golden years (1970–1985) of the rare-earth β-diketonates was the period when these compounds were frequently used as NMR shift reagents. In the 1990s, intense research activity on rare-earth β-diketonates started, now triggered by the application of these compounds as electroluminescent materials in OLEDs, as volatile reagents for chemical vapor deposition or as catalysts in organic reactions. The first rare-earth β-diketonates have been prepared by Urbain at the end of the 19th century, using tetrakis acetylacetonate complex of cerium (IV) and the hydrated tris acetylacetonate complexes of Ln(III), Gd(III) and Y(III) [82].

In 1993 Kido et al. synthesized red electroluminescent tris (theotyltrifluoroacetonate)Eu^{3+} ($Eu(TTA)_3$) complex, which is non volatile [83]. In 1994, a brighter red electroluminescence was observed using tris(dibenzoylmethanato) phenanthroline Eu^{3+}, $Eu((DBM)_3(Phen))$, as the emitting material. The second added ligand, phenanthroline, acts to saturate the coordination number of Eu ion and also to improve the fluorescence intensity, volatility, and stability of the Eu complex [84].

Uekawa et al. [85] studied PL excitation of Eu complexes with different ligands like TTA: Thenoyl Trifluro Acetone, FlHA: 1-(2-fluorenyl)-4, 4, 5, 5, 6, 6, 6-heptafluoro-1, 3, Hexanedione, DNM: Di (2-naphthoyl) methane TPD (N,N′-biphenyl-N,N′-(3-methyl phenyl)-1,1′-biphenyl-4,4′-diamine). In 1998, Rodriguez-Ubis et al. discovered a simple ligand based on acetophenone bearing excellent quantum yield for the excitation of Eu^{3+} and Tb^{3+} [86]. Tetra-acid ligand derived from acetophenone was synthesized and luminescence properties of their chelates with Eu(III) and Tb(III) were evaluated in aqueous and methanol solutions. These complexes have excellent quantum yields of triplet sensitization of lanthanide luminescence.

Poly(3-alkylthiophene)s (PATs)and other polythiophene (PTs) are popular red electroluminescent materials because of their ease in tunability [87,88], good solubility and chemical stability. Properties of these materials can be changed by structural modification, which allows the control of the torsion of the main chain and thus the adjustment of the effective conjugation length [89–94].

In 1999 Hao et al. studied the luminescence behavior of $Eu(TTA)_3$ doped in the sol–gel films [95]. The $Eu(TTA)_3$ doped sol–gel films can be formed by dip-coating of the $EuCl_3$ and TTFA (Thenoyl trifluoro acetone) co-doped solution. The luminescence intensity of the $Eu(TTA)_3$ doped sol–gel films was significantly increased with the increasing of film thickness. Miyamoto et al. synthesized a Eu(III) β-diketonate complex, $Eu(DBM)_3Phen$ [96]. Thin film of $Eu(DBM)_3Phen$ doped with phosphorescent material in OLED showed excellent electroluminescent spectra at room temperature which depends on the host materials, energy transfer from triplet states of the phosphorescent materials to the ligand triplet state of the Eu complex.

Fu et al. [97] synthesized and studied the luminescent properties of the ternary europium complexes with ligands thenoyltrifluroacetone (TTA) and Phenanthroline (Phen) incorporated into SiO_2 polymer matrix by a sol–gel method. The lifetime of rare earth ion Eu^{3+} in SiO_2/PVB gel matrix doped with $Eu(TTA)_3Phen$ was found to be longer than in pure $Eu(TTA)_3Phen$ powder and solvated $Eu(TTA)_3Phen$ in ethanol solution.

Eu complexes with β-diketonate and phenanthroline were incorporated in the polyphenylene polymer matrix. The thin film was obtained by spin casting. The efficient energy transfer from the polymer to the Eu complex resulted in complete quenching of the broad emission of the polymer, and a pure red Polymeric LEDs were reported [98,99]. In 2001 Yang et al. fabricated a red single-layer type of EL device based on a copolymer containing carbazole, Eu complex, and methyl methacrylate [100].

Adachi eta al in 2000 investigated the energy mechanism for energy transfer leading to electroluminescence of lanthanide complex $Eu(TTA)_3Phen$ doped into 4-4′-N,N′-dicarbozole-biphenyl (CPB) host. They achieved maximum external quantum efficiency of 1.4% at a current density of 0.4 mA/cm^2 with the device structure of anode/HTL/$Eu(TTA)_3$ Phen (1%):CPB/ETL/cathode [101].

In 2001 Chen et al. [102] used series of tris-(8-hydroxyquinoline) metal chelates with central metal ions of Al^{3+}, Ga^{3+}, In^{3+} as the host materials. A red fluorescent dye, 4-(dicyanomethylene)-2-t-butyl-6-(8-methoxy-1,1,7,7-tetra methyljulolidyl-9-enyl)4H-pyran (DCJMTB) was used as the emitter or guest dopant material. The doped devices with Gaq_3 as the host materials produced high efficiencies and saturated red colour chromaticity. The device with 1% DCJMTB doped in Gaq_3 showed a current efficiency of 2.64 cd/A. The colour coordinates of the Gaq_3:1% DCJMTB device was found to be (0.63,0.36).

In 2002 Ma et al. [103] synthesized a novel red luminescent material N,N-bis{4-[2-(4-dicyanomethylene-6-methyl-4H-pyran-2-yl) ethylene]phenyl}aniline (BDCM) with two (4-dicyanomethylene)-4H-pyran electron-acceptor moieties and a triphenylamine electron-donor moiety for application in OLED's. The three-layered EL device with the structure ITO/CuPc/DPPhP/BDCM/Mg:Ag has a turn-on voltage of less than 4 V, which suggests that BDCM has an excellent electron injection property, a bright luminance of 582 cd/m^2 at 19 V.

In 2003, Hu et al. [104] adopted emulsifier-free emulsion polymerization to synthesize rare earth containing submicron polymer particles under microwave irradiation. To control the size and distribution of the particle, the relationship between reaction time, monomer content, and particle radius was studied for the polymerization of methyl methacrylate (MMA) in the absence and

presence of rare earth ions, with water as solvent. For particles containing rare earth ions, characterization shows that mole percentage of Eu(III) ion in the surface layer with a thickness of 5 nm, estimated from X-ray photo electron spectroscopy (XPS), is always larger than the value estimated by inductively coupled plasma atomic emission spectrometer (ICP-AES) for the whole particle, indicating that surface enrichment of rare earth ions took place during the polymerization.

In 2004, Liu et al. [105] synthesized europium doped ternary complexes namely $Eu(DBM)_3$phen, $Eu(DBM)_3$(DB-bpy), $Eu(DBM)_3$ (DN-bpy) and $Eu(DBM)_3$biq (DBM, Phen, DB-bpy, DN-bpy and biq refer to Dibenzoylmethane, 1,10-phenanthroline, 4,4′-Di-*tert*-butyl-2,2′-dipyridyl, 4,4′-Dinonyl-2,2′-dipyridyl and 2,2′-Biquinoline, respectively) in PMMA matrix. The luminescence properties of the composites were investigated by emission spectroscopy and lifetime measurements. The composites formed by Eu(III) complexes, exhibit strong luminescence and similar emission spectral characteristics. Whereas, $Eu(DBM)_3$biq shows large differences in its luminescence spectrum compared to those of other complexes. Investigations on Eu doped β-diketonates Eu(III) ions in the doped $Eu(DBM)_3$/PMMA systems have two distinct symmetric sites and the emission band changes greatly with the compositions. Eu(III) in the $Eu(BA)_3$/PMMA systems gives only one symmetric site in the doped systems and the emission band changes slightly with the compositions [106].

Ohmori et al. [107] employed two kinds of material systems utilizing energy transfer and energy confinement: one, a co-doped OLED, which consists of two different kinds of materials doped in the emissive layer, and the other type a europium (Eu) complex (1,10-phenanthroline)-tris (4, 4, 4-trifluoro-1-(2-thienyl)-butane-1,3-dionate) europium (III), $Eu(TTA)_3$phen doped in poly(N-vinylcarbazole) (PVK). Red light emission at 614 nm was obtained with efficient emission relaxation in Eu^{3+} sites.

In 2006, Lee et al. [108] synthesized Eu containing nano particles using the ultra-dilute solution method. The size of nano particles containing Eu was 30–150 nm and they were soluble in common organic solvents. A study of the dependence of emission intensities of the Eu-containing nano particles on the Eu content showed that the emission intensities increased linearly with increasing europium content. No significant emission concentration quenching phenomenon was observed when europium content was in the range of 0–9.5 mol%.

Jiu et al. [109] studied the fluorescence enhancement of $Eu(DBM)_3$Phen as well as $Tb(DBM)_3$Phen in PMMA. A combinatorial methodology was adopted to allow rapid optimization of the fluorescence enhancement conditions of thin-film samples in arrays of micro wells. Based on $Eu(DBM)_3$Phen doped PMMA, three material libraries were generated in order to compare the effects of species identity and $Tb(DBM)_3$Phen content to the effect of other complexes containing enhancing ions (La^{3+}, Gd^{3+}, Dy^{3+}, Y^{3+}, Ce^{3+}) on the luminescence efficiency of the Eu^{3+} complex in PMMA. The fluorescence enhancement of $Eu(DBM)_3$Phen in PMMA is considered to originate by the process of intra molecular and intermolecular energy transfer.

In 2006 Qu et al. [110] synthesized two novel polymers PQP (poly(3, 7-N-octyl phenothiozinyl cyano terephthalylidene)) and PQM (poly(3, 7-N-octyl phenothiozinyl cyanoisophthalylidene)) containing phenothiazine for application in red and orange light-emitting diodes. The single-layer EL devices of ITO/PQP (or PQM)/Mg: Ag and multi-layer devices of ITO/PQP (or PQM): N, N′-diphenyl-N, N′-bis(3-methylphenyl)-[1, 1′-biphenyl]-4, 4′-diamine (TPD) (44 nm)/2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline (BCP, 5 nm)/tris(8-hydroxyquinolinato) aluminium (AlQ_3, 20 nm)/Mg:Ag were fabricated. The EL spectra from the devices based on PQP, PQM peaked at the wavelength of 664 nm, 608 nm with maximum brightness of 60 cd/m^2, 150 cd/m^2 at the applied voltage of 17 V and 14 V, respectively.

In 2008 a dinuclear Eu(III) complex $Eu_2(btbt)_3 \cdot 4H_2O \cdot CH_3CH_2OH \cdot N(CH_2CH_3)_3$ was synthesized by Park et al. [111] (btbt is 4,4-bis (4″,4″,4″,-trifluoro-1″,3″-dioxobutyl)-*o*-terphenyl). The complex emits the characteristic red luminescence of Eu^{3+} ion due to the $^5D_0 \rightarrow {}^7F_J$ (J=0, 1, 2, 3, 4) transitions under 395 nm light excitation with good luminescent quantum efficiency around 32% and exhibits high thermal stability till 337 °C. Bright red LEDs were fabricated by coating the complex onto a 395 nm emitting InGaN chip. When the mass ratio of the red phosphor to the silicone is 1:30, the efficiency of the fabricated LEDs with the europium complex was 0.98 lm/w with high CRI and CIE chromaticity coordinates (0.6, 0.3).

Khizar-ul Haq et al. in 2009 fabricated efficient red organic light-emitting diodes based on a wide band gap material 9,10-bis (2-naphthyl) anthracene (ADN) doped with 4-(dicyano-methylene)-2-t-butyle-6-(1,1,7,7-tetramethyl-julolidyl-9-enyl)-4H-pyran (DCJTB) as a red dopant and 2,3,6,7-tetrahydro-1,1,7,7,-tetramethyl-1H,5H, 11H-10(2-benzothiazolyl)quinolizine-[9,9a,1gh]coumarin (C545T) as an assistant dopant. The C545T dopant did not emit by itself but did assist the energy transfer from the host (ADN) to the red emitting dopant through cascade energy transfer mechanism. This approach significantly improved the EL efficiency of OLEDs. They achieved a significant improvement regarding saturated red color when a polar cohost emitter (Alq_3) was incorporated in the matrix [ADN:Alq_3]. Since ADN possesses a considerable high electron mobility, co-host devices with high concentration of ADN ($>70\%$) exhibited low driving voltage and high current efficiency as compared to the devices without AND with current efficiency of 3.6 cd/A, CIE coordinates of [0.618, 0.373] and peak wavelength at 620 nm at a current density of 20 mA/cm^2 [112].

In 2009 Lyu et al. fabricated highly efficient phosphorescent OLEDs using a non conjugated silicon-cored spirobifluorene derivative (SBP-TS-PSB) as a host material for the red phosphorescent Ir(III) complexes. Three phosphorescent guests, $(piq)_3Ir$, $(piq)_2Ir$ (acac), and $(btp)_2Ir(acac)$ were doped in the SBP-TS-PSB host and the device performances were investigated. The external quantum efficiencies, power efficiency and CIE color coordinates obtained from $(piq)_2Ir(acac)$, $(piq)_3Ir$, and $(btp)_2Ir(acac)$ based devices are 14.6%, 10.3 lm/W (0.68, 0.32) at J=1.5 mA/cm^2, 13.5%, 7.8 lm/W (0.66, 0.32) at J=1.3 mA/cm^2, and 9.9%, 7.0 lm/W (0.66, 0.31) at J=0.5 mA/cm^2, respectively. [113]

Seo et al. in 2009 fabricated novel red OLEDS using phosphorescent heteroleptic triscyclometalated iridium complex, bis(2-phenylpyridine)iridium(III)[2(5′-methylphenyl)-4-diphenylquinoline] [$Ir(ppy)_2(dpq\text{-}5CH_3)$], based on 2-phenylpyridine (ppy) and 2(5′-methylphenyl)-4-diphenylquinoline (dpq-5CH_3) ligand. ppy ligand in heteroleptic iridium complexes plays an important role as sensitizer in the efficient energy transfer from the host (CBP;4,4,N,N′ dicarbazolebiphenyl) to the luminescent ligand (dpq-5CH_3), demonstrating high efficiency through the sensitizing ligand. The device containing $Ir(ppy)_2(dpq\text{-}5CH_3)$ produced red light emission of 614 nm with maximum luminescence efficiency and power efficiency of 8.29 cd/A at 0.09 mA/cm^2 and 5.79 lm/W at 0.09 mA/cm^2, respectively [114].

In 2011 Thejo Kalyani et al. [115] fabricated red OLEDs with $Eu_xY_{(1-x)}(TTA)_3$Phen organic complex as emissive layer (TTA=thenoyltrifluoro-acetone, phen=1,10-phenanthroline, x=0.4 and x=0.5). The mechanism of energy transfer leading to EL of a lanthanide complex, doped into TPBi(1,3,5-tris(N-Phenyl-benzimidizol-2-yl) benzene host at 15 wt% of host was investigated. The band structure and device architecture of device I and device II are shown in Figs. 6 and 7, respectively .With the device structure of anode/hole transport layer/$Eu_xY_{(1-x)}(TTA)_3$Phen(15%):TPBi/electron transport layer/cathode, maximum luminescence of 185.6 cd/m^2 and 44.72 cd/m^2 was obtained from device I and II, respectively.

Lanthanide based organic luminescent complexes $La_{(1-x)}Eu_{(x)}TTA_3$ Phen (La: Lanthanum, x=0.2, 0.4, 0.5, 0.6, 0.8) were synthesized,

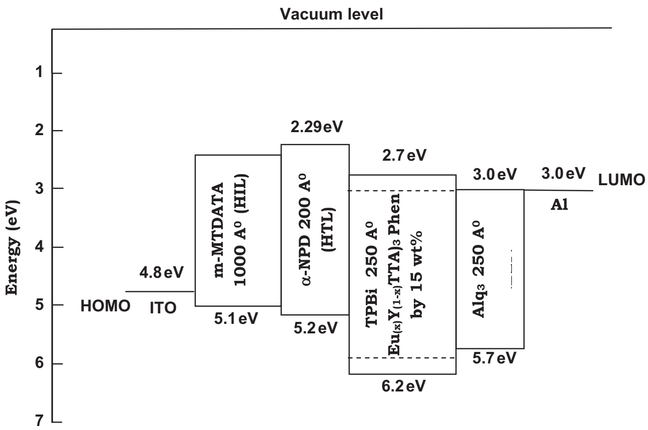


Fig. 6. The band structure of device I and device II [114].

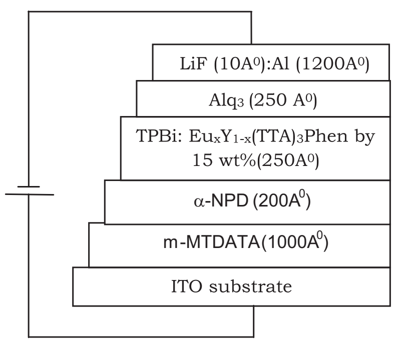


Fig. 7. Structure of fabricated OLED devices [114].

maintaining stichiometric ratio by Malhar et al. Broad absorption peak was observed at 349 nm for all the complexes with no shift in the peak wavelength, indicating that absorption peak is independent of metal ion but depends on aromatic group of the β-diketone ligand (TTA). Prominent sharp red emission line was observed at 612 nm wavelength, when excited at 360 nm light. Maximum emission wavelength was observed in $La_{0.6}Eu_{0.4}TTA_3Phen$ [116].

Europium β-diketonate complexes $Eu_xRe_{(1-x)}TTA_3Phen$, (Re= Y/Tb Y: Yttrium, Tb: Terbium TTA $x=0.5$) were dispersed in Polystyrene (PS) matrix by Phatak et al. [117]. Absorption spectra of all these complexes have two absorption peaks at 280 and 360 nm attributed to n–π and π–π^* transition of TTA. The composites formed by the three complexes $Eu(TTA)_3Phen$, $Eu_{0.5}Tb_{0.5}(TTA)_3Phen$, $Eu_{0.5}Y_{0.5}(TTA)_3Phen$ doped in PS show significant changes in their luminescence spectra.

EL cells were made out of novel red emitting organic luminescent complexes, namely $Eu_{0.5}Ln_{0.5}$ $(TTA)_3$ Phen (Eu: europium, Ln:Y/Tb, Y: yttrium, Tb: terbium, TTA: thenoyl tri fluoro acetone, Phen: phenanthroline) by sandwiching it between indium tin oxide (ITO) and aluminum(Al). Turn on voltage of both the devices was found to be 9 V. These devices emit intense red emission at 611 nm, proving their potential applications as organic light emitting diodes and displays [118].

10.2. Green light emitting materials and OLEDs

Bright green emission from aluminum tris(8-hydroxyquinolinate) (Alq_3) thin film organic layers was demonstrated by Tang and Vanslyke in 1987 [25].

In 1990, Kido et al. reported a double layer OLED containing Tb-tris-(acetylacetonato), $Tb(acac)_3$ as green light emitting material, N, N′-diphenyl-N, N′-bis(3-methylphenyl)1,1′-biphenyl-4,4′diamine (TPD) as hole-transport layer with device structure, ITO/TPD/Tb$(acac)_3$/Al. Strong emission peak at 544 nm peak, corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition of the Tb^{3+} ion was observed [12].

Kasim et al. [119] synthesized a new conjugated polymer, poly (2,bquinoline vinylene) (PQV), which exhibited maximum fluorescence at 515 nm when excited at 430 nm. PLEDs were constructed with ITO/PQV/Al configuration, broad emission peak at 530 nm was observed.

A thermally stable Tb-tris(tetradecylphethalate) phenanthroline complex $Tb(MTP)_3Phen$ was prepared and used as green emitting layer by Ma et al. in 1999 [120]. Its chemical structure is shown in Fig. 8.

Multilayered EL device consisting of ITO/poly(*p*-phenylenevinylene) (PPV) as a hole transfer layer/PVK doped with Tb$(MTP)_3$(Phen)/Alq_3/Al was designed by Lin et al. in the year 2000. The sharp green emission was observed with luminance of 152 cd/m^2 at 24 V with poor external quantum efficiency of 0.017% using Tb complex was doped with PBD and PVK with a double-device structure, ITO/PVK:PBD:Tb$(MDP)_3$/Alq_3/Al, was also fabricated [121].

Phosphorescent dendrimers with *fac*-tris(2-phenyl-pyridyl) iridium(III) cores, biphenyl based dendrons and 2-ethylhexyloxy surface groups, which emit green light were reported by Markham et al. The solution processable green phosphorescent dendrimers have been used to fabricate highly efficient single layer devices, as well as bi-layer OLEDs giving efficiencies of up to 16% with 40 lm/W at 400 cd/m^2 [122–124].

In 2003 Palilis et al. [125] reported the performance of molecular organic light-emitting diodes (MOLEDs) using novel fluorescent silole derivatives as highly efficient blue and green-emitting organic materials. Three silole derivatives, namely 2,5-di-(3-biphenyl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene(PPSPP), 9-silafluorene-9-spiro-1′-(2′,3′,4′,5′-tetra phenyl)-1′H-silacyclopentadiene (ASP) and 1,2-bis(1-methyl-2,3,4,5,-tetra phenyl sila cyclo pentadienyl) ethane (2PSP), with high solid-state photoluminescence quantum yields of 0.85, 0.87 and 0.94, respectively, were used as emissive materials. High electron mobility silole derivative, 2,5-bis(2′,2″-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene(PyPySPyPy), was also used as the electron transport material. MOLEDs using these siloles as emitters and *N,N*′-diphenyl-*N*, *N*′-(2-napthyl)-(1,1′-phenyl)-4,4′-diamine (NPB) or *N,N*′-diphenyl *N,N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′diamine (TPD) as the hole transport material show low operating voltages of 4–4.5 V at a luminance of 100 cd/m^2 and high external electroluminescence (EL) quantum efficiencies of 3.4–4.1% at 100 A/m^2. Structure of synthesized complexes and device structure of the fabricated OLEDs is shown in Fig. 9.

Mishra et al. reported a bluish green emission from OLED based on aluminium complex, bis(2-methyl 8-hydroxiquinoline) aluminium hydroxide ($Almq_2OH$) as an emissive material [126].

In 2005 Hwang et al. developed a stable green OLED using an Al–Cu alloy as a cathode material. The device structure is shown in Fig. 10, where CF*x*, *N,N*′-bis-s1-naphthyld-*N,N*′-diphenyl,1,1′-biphenyl- 4,4′-diamine (NPB), tris(s8-quinolinolato)aluminium(Alq_3), and lithium acetate (CH_3COOLi) were used as the hole injection material, hole-transport material, light-emitting material, and electron-injection material, respectively [127].

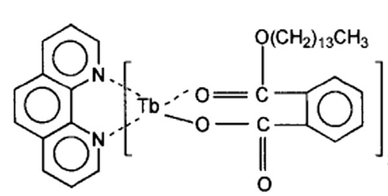


Fig. 8. Chemical structure of $Tb(MTP)_3Phen$. Reproduced from [119].

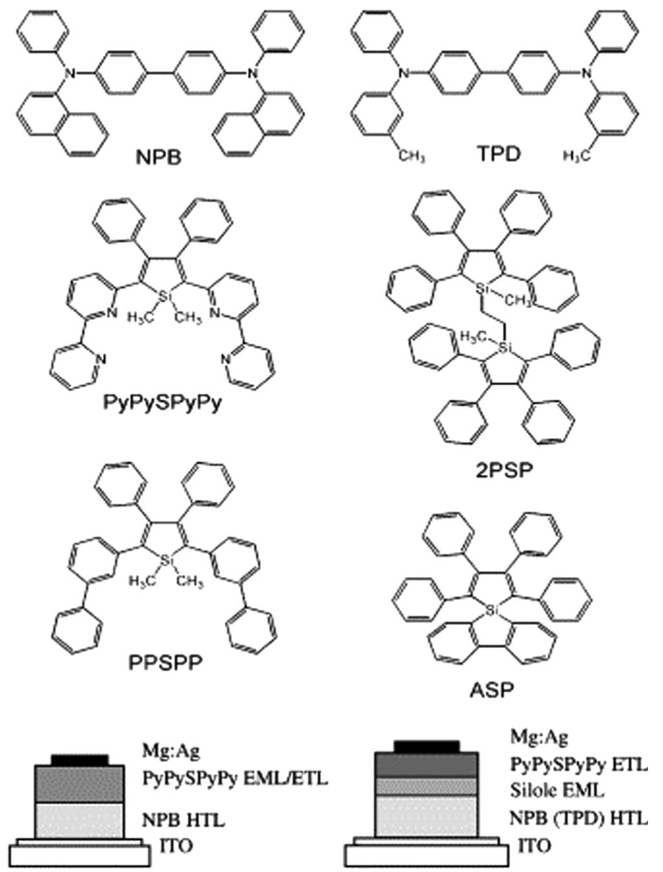


Fig. 9. Structure of synthesized complexes and device structure of the fabricated OLEDs by Leonidaset al. [125].

Ku et al. reported highly efficient non-doped green OLED by incorporating a novel 9,9-diarylfluorene-terminated 2,1,3-benzothiadiazole (DFBTA), which exhibits an excellent solid state photoluminescence quantum yield of about 81% The optimal device: ITO/DPAInT$_2$/DPAInF/TCTA/DFBTA/Alq$_3$/LiF/Al displayed impressive device characteristics, with maximum external quantum efficiency of 12.9 cd/A [128].

In 2010 Cho et al. [129] synthesized Ir(Cz-ppy)$_2$(Cz-Fppy)$_1$, Ir(Cz-ppy)$_1$(Cz-Fppy)$_2$, Ir(Cz-Fppy)$_3$ and Ir(Cz-ppy)$_3$ which exhibited green emission at 515, 511, 496 and 520 nm, respectively.

Liu et al. in 2009, investigated highly efficient phosphorescent OLEDs [130] based on an orange-red emission iridium complex as the guest and five green emission iridium complexes as the host material, respectively.

With cationic iridium complexes as dopants and poly(*N*-vinylcarbazole) as host, Lei et al. [131] fabricated highly efficient blue-green to red and white organic light-emitting diodes (WOLEDs) by solution process. In single-layer OLED devices, electron-trapping by complexes dominates the device performance. Complexes with cyclometalated 2-phenylpyridine ligands showed better device performance compared with those containing cyclometalated 2-(2,4-difluorophenyl)pyridine ligands. With the addition of an electron transporting and exciton blocking layer, the devices showed improved performances, achieving peak current efficiencies of 24.3, 25.3, 20.5, and 4.2 cd/A for the blue–green, green, yellow, and red electroluminescence, respectively. White OLEDs have been fabricated by co-doping blue–green and red–emitting complexes, attaining a peak current efficiency of 20.7 cd/A.

High efficiency green OLEDs were fabricated from solution processed ambipolar blends of electron and hole transport polymer hosts doped with green light emitting iridium complex sandwiched between HTL and ETL. The ambipolar host blends of bis-oxadiazole functionalized poly(norbornene) electron transport materials and poly(N-vinyl carbozole). An external quantum efficiency of 13.6% and a maximum luminous efficiency of 44.6 cd/A at 1000 cd/m^2 with turn on voltage of 5.9 V were obtained [132].

Alq$_3$ and Tb$_x$Al$_{(1-x)}$q$_3$ have been synthesized (where x=0.1, 0.3, 0.5, 0.7 and 0.9) and their blended films with PMMA and PS at different percentage weight (wt%) concentrations (0.1, 1, 5, 10, 25 and 50 wt%) have been prepared by Yawalkar et al. [133]. The synthesized metal complex shows bright emission of green light with blue light excitation (440 nm), find applications in blue chip-excited OLEDs for the newly developed wallpaper lighting technology.

10.3. Blue light emitting materials and OLEDs

Among the three primary RGB colors, the synthetic protocols and fabrication methods of green and red phosphors meet the necessary requirements. Conversely, the design and fabrication of blue phosphors and ensuing devices is still an ongoing challenge and hence review on blue light emitting materials and devices fabricated so far.

In 1992, Grem et al. for the first time reported on blue electroluminescence from OLEDs containing poly(*p*-phenylene) (PPP) [134].

A wide range of oligo(*p*-phenylenevinylene)s with alkyl [135–138] or alkoxy [139–144] substituents have been synthesized. Oligo(*p*-phe-nylene)s have been used as blue emitters [145–152] in electroluminescent devices, which exhibit high-fluorescence quantum yields.

Tao et al. [153], reported the blue emitter LiB(qm)$_4$ in the device structure of ITO/PVK:NPB (50 nm)/LiB(qm)4 (60 nm)/Mg:Ag. Power efficiency and the luminance of the device were 1.3 lm/W and 6900 cd/m^2, respectively.

Li et al. prepared Y, La, and Gd ion complexes with M(acea)$_3$ (Phen) [154]. However, these complexes were used as electron-transporting materials for the organic emitter, *N*,*N*′-bis(1-naphthyl-1, 1′-biphenyl-4,4′-diamine)(NPB) with OLED structure ITO/NPB/M (acea)$_3$ (Phen)/Mg:Ag.

Hong et al. were the first to use Tm^{3+} (Thulium) ion in OLEDs [155]. They prepared a tris(acetylacetonato)-monophenanthroline Tm complex and double-layer cell with anatomy ITO/PVK/Tm complex/Al.

Liu et al. in 2001 [156] reported the blue emitter Bepp$_2$ (Hydroxyphenyl-pyridine Beryllium complex). The Bepp$_2$ was put in two differently structured devices: (1) ITO/NPB (60 nm)/Bepp$_2$ (50 nm)/LiF (1 nm)/Al (200 nm) and (2) ITO/CuPc (15 nm)/NPB (60 nm)/Bepp2 (50 nm)/LiG (1 nm)/Al (200 nm) to study their PL.

Fluorene-based blue electroluminescent polymers Poly[9,9′-bis (2-ethylhexyl)fluorene-2,7-diyl] end-capped with N,N′-bis(4-methylphenyl)-N-phenylamine [157] and Poly(9,9′-dioctylfluorene-2,7-diyl) (PF8, PFO) [158] also showed blue emission.

OLEDs fabricated with FIrN4 ((iridium (III) bis(4,6 difluorophenylpyridinato)(5-(pyridin-2-yl)-tetrazolate) as dopant in mCP (1,3-bis(9-carbazolyl)benzene), exhibit near-saturated blue electrophosphorescence with CIE coordinates of (0.15, 0.24) [159].

Cheng et al. [160] fabricated pure blue OLED with CIE coordinates of (0.1638, 0.094) at 16 V using a derivative of oligo(phenylenvinylene), 2,5-diphenyl-1, 4-distyrylbenzene with two *trans*-double bonds, as a light-emitting layer. Maximum luminance of 1400 cd/m^2 and a maximum luminous efficiency of 1.18 cd/A by introducing of perylene as a dopant in the light-emitting layer, luminance dramatically enhanced to 5500 cd/m^2 and 3.18 cd/A.

Ding et al. [161] fabricated blue OLEDs using undoped 9,10-di(2-naphthyl)anthracene (ADN) as the emitting layer, N,N^1-diphenyl-N, N^1-bis(3-methylphenyl)-1,10-biphenyl-4,40-amine (TPD) as the hole

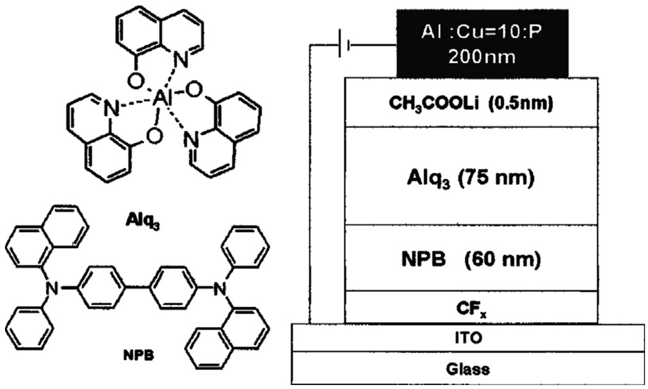


Fig. 10. Structure of Alq_3, NPB and device structure of the fabricated device by Hwang et al. [127].

transporting layer, and one of tris-(8-hydroxy-quinolinato) aluminum (Alq_3), 4,7-diphenyl-1,10-phenanthroline (Bphen) and 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) as the electron transporting layer.

Zheng developed efficient OLEDs by doping fluorescent- and phosphorescent-type emitters individually into two different hosts separated by an interlayer to form a fluorescence-interlayer-phosphorescence (FIP) emission architecture. Blue OLED with FIP emission structure comprising p-bis(p-N,Ndiphenylaminostyryl) benzene (DSA-Ph) and bis [(4,6-di-fluorophenyl)-pyridinate-N, C2′]picolinate (FIrpic) exhibited a peak luminance efficiency of 15.8 cd/A at 1.54 mA/cm^2 and a power efficiency of 10.2 lm/W at 0.1 mA/cm^2 [162].

Khizar-ul-Haq et al. [163] synthesized blue organic light-emitting diodes with 9,10-bis(2-naphthyl)-2-t-butylanthracene (TBADN) doped with (3 wt%) P-bis(P-N,N-diphenyl-aminostyryl) benzene (DSA-Ph) as an emitting layer, the typical device structure was ITO/HIL (5 nm)/NPB (25 nm)/EML (35 nm)/ETL (15 nm)/LiF (0.8 nm)/Al (100 nm). At the current density of 20 mA/cm^2, its driving voltage and power efficiency was 5.2 V and 4.2 lm/W, which was independently reduced by 48% and improved by 44% compared with those of the m-MTDATA/Alq_3 based one, respectively.

Pu et al. in 2010 [164] synthesized hole-transporting arylamino-9, 10-diphenylanthracene derivatives by C–N cross coupling with palladium catalyst. These materials showed higher glass transition temperatures (135–177 °C). Alq_3 based green light emitting devices containing the arylamino-9, 10-diphenylanthracene derivatives as hole transport layers were fabricated.

A new series of blue fluorescent emitters based on *t*-butylated bis(diarylaminoaryl) anthracenes were synthesized by Lee et al. [165]. Into these blue materials, *t*-butyl groups were introduced to prevent molecular aggregation between the blue emitters through steric hindrance and reduce self-quenching. To improve efficiency, multilayered OLEDs were fabricated into a device structure of: ITO/NPB(50 nm)/blue emitters doped in ADN(30 nm)/Alq_3(20 nm)/Liq (2 nm)/Al(100 nm). All devices showed efficient blue emissions. One of the device exhibited highly efficient sky blue emissions with a maximum luminance of 11,060 cd/m^2 at 12.0 V and respective luminous and power efficiencies of 6.59 cd/A and 2.58 lm/W at 20 mA/cm^2. The peak wavelength of the electroluminescence was 468 nm with CIE coordinates of (0.159, 0.198) at 12.0 V. In addition, a deep blue device with CIE coordinates of (0.159, 0.151) at 12.0 V showed a luminous efficiency of 4.2 cd/A and power efficiency of 1.66 lm/W at 20 mA/cm^2.

RGB phosphorescent *p–i–n* homojunction devices by using a series of bipolar host materials, including 2,6-bis(3-(carbazol-9-yl) phenyl) pyridine (2,6DCzPPy), 3,5-bis(3-(carbazol-9-yl)phenyl) pyridine (3,5DCzPPy) and 4,6-bis(3-(carbazol-9-yl)phenyl) pyrimidine (4,6DCzPPm) were demonstrated by Cai et al. [166]. Homojunction

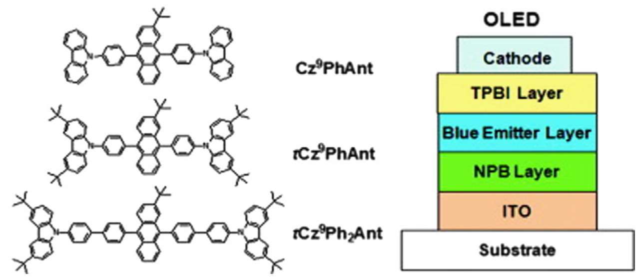


Fig. 11. Chemical structures of anthracene derivatives and device structure of blue OLEDS fabricated by Chen et al. [167].

devices comprise a MoO_3-doped host as a hole transport layer, and a Cs_2CO_3-doped host as an electron transport layer. Emission layer consists of a host doped with iridium(III) bis(4,6-(di-fluorophenyl) pyridinato-*N*,$C^{2\prime}$) picolinate (FIrpic) for blue, *fac*-tris(2-phenylpyridine) iridium ($Ir(ppy)_3$) for green, and tris(1-phenylisoquinolinolato-C^2,*N*)iridium(III) ($Ir(piq)_3$) for red devices. External quantum efficiencies of 12.9% for the 35DCzPPy-based blue, 9.5% for the 4,6DCzPPm-based green, and 8.5% for the 4,6DCzPPm-based red devices were achieved at 100 cd/m^2.

Chen et al. [167] synthesized three anthracene derivatives featuring carbazole moieties as side groups-2-*tert*-butyl-9,10-bis [4-(9-carbazolyl)phenyl]anthracene (Cz^9PhAnt), 2-*tert*-butyl-9,10-bis{4-[3,6-di-*tert*-butyl-(9-carbazolyl)]phenyl}anthracene(*t*Cz^9Ph Ant), and 2-*tert*-butyl-9,10-bis{4′-[3,6-di-*tert*-butyl-(9-carbazolyl)] biphenyl-4-yl}anthracene (*t*Cz^9Ph_2Ant) for use in blue OLEDs with high glass-transition temperature of 220 °C as shown in Fig. 11. They exhibited strong blue emissions in solution, with high quantum efficiency of 91%. Blue emission from bis(4,6-difluorophenyl-pyridinato-N,C_2^1) (picolinate) irridium (III) (Firpic) was studied by Lai et al. [168].

10.4. White light emitting materials and OLEDs

Differing from the other colours the white emission from OLEDs have an advantage that it can be used as back light in LCDs to produce full colour display using micro pattered colour filter [169]. Materials used for these devices include conjugated polymers, metal complexes [170] and organic dyes. There are several devices designed from which the white light has been observed a broad band covering the whole VIS region [171,75]. In order to achieve maximum efficiency and high colour purity, white light should be composed of three discrete peaks in the blue, green and red region. The first white OLED was fabricated by Kido et al. in 1994 [75]. This device contained red, green and blue light emitting compounds that together produce white light with efficiency less than 1 lm/W.

Deshpande et al. in 1999 obtained white light emission by the sequential energy transfer between different layers. The device configuration was ITO/α-NPD/α-NPD: DCM_2(0.6–8 wt%)/BCP/Alq_3/Mg:Ag (20:1)/Ag. 4,4′ bis (N-(1-napthyl-N phenylamino)) biphenyl (α-NPD) was used as a hole injection layer, α-NPD: DCM_2 (2, 4-(dicyanomethylene)-2-methyl-6-(2-(2, 3, 6, 7-tetrahydro-1H, 5H benzo(I, j)quinolizin-8-yl) vinyl)-4H-pyran) layer was used as HTL as well as an emitting layer, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was deposited for blocking holes, Alq_3 was used as ETL and Mg:Ag alloy followed by a thick layer of Ag was deposited as the cathode [172].

Use of phosphorescent dopants as the emitters in a segregated layer WOLED was first demonstrated by D'Andrade et al. in 2001 [173] with the device structure ITO/poly(ethylene-dioxythiophene):poly(styrene sulphonic acid) (PEDOT:PSS)/4,4′-bis [N-(1-napthyl)-N-phenylamino]biphenyl (α-NPD) 30 nm/4,4′-N, N′-dicarbazolebiphenyl(CBP) 20 nm:6 wt% iridium(III)bis(4,6-di-fluorophenyl)-pyridinato-N,C2) picolinate (FIrpic),/CBP layer 8 wt%:bis (2-(2′-benzo [4,5-a]thienyl)pyridinato-N,C3) iridium (acetylacetonate)

($Btp_2Ir(acac)$), 2 nm/CBP 8 wt% bis(2-phenyl benzothiozolato-N,C2′) iridium(acetylacetonate) ($Bt_2Ir(acac)$)2 nm/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was the final organic layer and served as both a blocking layer and an electron transport layer (ETL). Efficiency of about 5.2% external quantum efficiency, CIE coordinates of (0.35, 0.36), a CRI of 83 and peak brightness over 30,000 cd/m^2 was achieved.

Kido et al. [170] used Tb^{3+} and Eu^{3+} complexes to achieve multilayer white OLEDs with Eu $(aca)_3$Phen binuclear complexes as the emitting layer. These devices emits bright white light with more uniform and more energy efficient than that emitted by fluorescent lights.

A white light emitting device was fabricated by Xiao et al. in 2005, with a structure of ITO/NPB/BCP/Alq_3/LiF/Al. The hole blocking layer (BCP) results in a mixture of lights from NPB molecules (blue-light) and Alq_3 molecules (olivine-light), thereby emitting white-light. Maximum brightness of 5740 cd/m^2, with EL efficiency of 2.12 cd/A at the applied voltage of 18 V was achieved [174]. The schematic cross section of fabricated OLED structure is shown in Fig. 12.

In 2005 Tsou et al. fabricated white OLED by doping 1% DCM_2 in Bathocuproine (BCP) layer. The CIE coordinates (x, y) of the device are 0.32 and 0.32 respectively [175].

Gong et al. in 2005 reported high performance multilayer white light emitting PLEDs fabricated by using a blend of luminescent semiconducting polymers and organometallic complexes as the emission layer and water or ethanol soluble $PVKSO_3Li$ as the hole injection/transport layer and t-Bu-PBD-SO_3Na as the electron injection/electron transport layer [176].

Yu et al. in 2009 reported white LEDs using a blue InGaN LED pre-coated conjugated copolymer/quantum dots (QDs) composite (green-emitting Poly {(9,9-dioctyl-2,7-divinylenefluorenylene)-alto-co-(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene)}/red-emitting

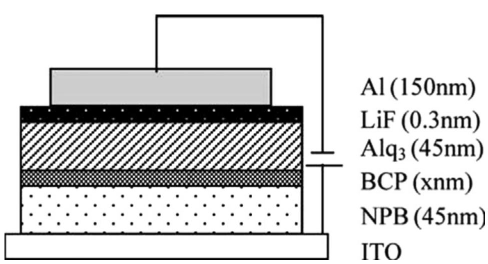


Fig. 12. The schematic cross section of fabricated OLED structure by Xiao et al. Reproduced from Ref. [170].

CdSe quantum dots) as a hybrid phosphor. The white LED of the hybrid phosphor containing 20 wt% QDs had a luminous efficiency of 44.2 lm/W at 20 mA with a CIE coordinate, color temperature and color-rendering index of (0.3297, 0.3332), 5620 K and 75.3 respectively [177].

Bright WOLEDs with single active layer has been demonstrated from blue emitting zinc complex bis(2-(2-hydroxyphenyl)benzoxazolate)zinc [$Zn(hpb)_2$] doped with orange luminescent 4-(dicyanomethylene)-2-methyl-6-(p-dimethyl-aminostyryl)-4H-pyran (DCM) dye. White light electroluminescence (EL) spectrum from $Zn(hpb)_2$ was achieved by adjusting the concentration of DCM dye. WOLED with a structure of ITO/α-NPD/$Zn(hpb)_2$:DCM (x%)/BCP/Alq_3/LiF/Al has been fabricated. The EL spectra with two peaks at 446 and 555 nm were obtained. The device emits white light at 10 V with CIE coordinates (0.27, 0.31) and brightness 1083 Cd/m^2. The maximum current efficiency of the device was 1.23 Cd/A at 9.5 V and maximum luminance reaches 2210 Cd/m^2 at 12 V [178]. Configuration of WOLEDS, its photograph and molecular structure of DCM dye and $Zn(hpb)_2$ are shown in Fig. 13.

Chang et al. reported high color rendering pure-white phosphorescent OLEDs by iridium complex Ir(dfbppy) $(fbppz)_2$ and a wide-band width yellow emitting osmium complex $Os(bptz)_2$ (dppee).They achieved CRI of 81 and CIE coordinates close to the ideal white emission (0.33, 0.33) [179].

Tyagi et al. in 2010 demonstrated a WOLED by double layers of blue $Zn(hpb)_2$ and yellow Zn(hpb)mq emitting materials. It was observed that when the thickness of Zn(hpb)mq layer was increased the dominant wavelength shifts from bluish to yellowish region. CIE coordinates (0.29, 0.38) with a low turn on voltage (5 V) was achieved [180].

Chen et al. in 2010 [181] fabricated WOLEDs utilizing two primary color emitters without any additional blocking layer. ADN was deposited directly above the rubrene (Rb)-doped NPB yellow light emitting layer with a structure of ITO/2TNATA(20 nm)/NPB(20 nm)/NPB: rubrene(2%)(10 nm)/ADN(30 nm)/Alq_3(20 nm)/LiF(1n)/Al (100 nm), a white light with CIE coordinates (0.344,0.372) at a current density of 30 mA/cm^2 was generated.

In 2011 Hu et al. [182] reported a theoretical investigation of the white light emission from a single polymer system with simultaneous blue polyfluorene as host and orange (2,1,3-benzothiadiazole (BTD) based derivative as dopant emission. They employed quantum chemical approaches to study the variations in electronic and optical properties as a function of the chemical composition of the backbone in BTD based derivatives. The chemical structure of model polymers is shown in Fig. 14.

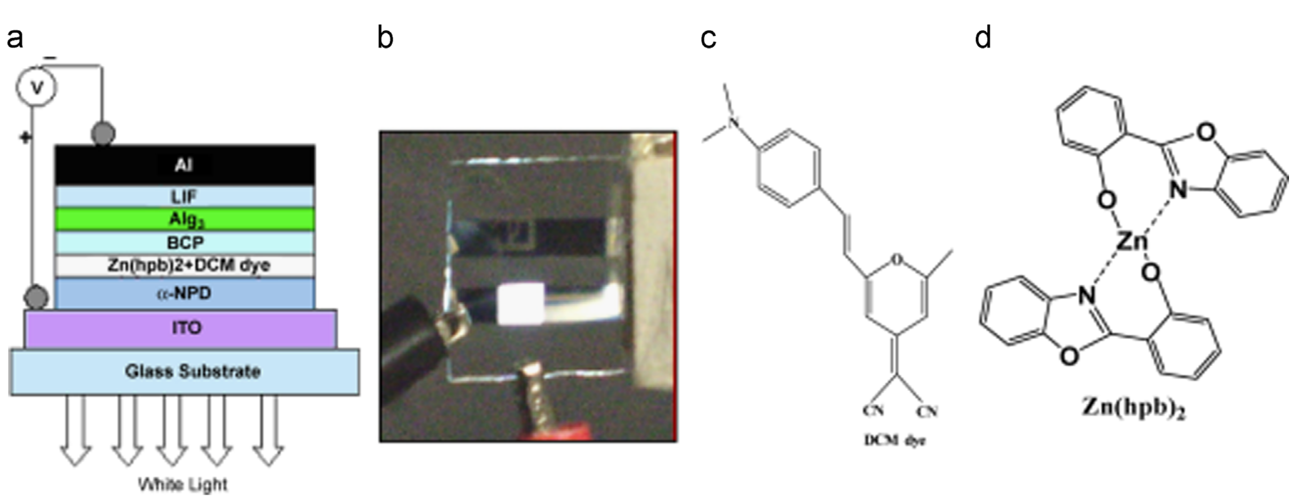


Fig. 13. (a) White organic light-emitting diodes configuration and (b) the photograph of WOLEDdevice and molecular structure of (c) DCMdye and (d) $Zn(hpb)_2$ [178].

In 2011, HoonSeo et al. [183] demonstrated hybrid white organic light-emitting diodes (HWOLEDs) on electroluminescent characteristics for codoped spacer ratio effect using *N,N′*-dicarbazolyl-3,5-benzene (mCP) and 4,7-diphenyl-1,10-phenanthroline (BPhen). They achieved external quantum efficiency of 6.01%, the power efficiency of 8.12 lm/W, and CIE coordinates of (0.37, 0.41) at 1000 cd/m^2.

A new class of charge neutral, strongly luminescent cyclometalated platinum (II) complexes supported by dianionic tetradentate ligand are synthesized by Lai et al. One of these platinum (II) complexes, Y-Pt, displays high PL quantum yield of 86% and EL efficiency of upto 52 lm W^{-1}, and is utilized as yellow phosphorescent dopant in the fabrication of white OLEDs [168].

11. Role of white OLEDs in solid state lighting

White OLEDs also have the true colour qualities of incandescent lighting, as they can be made into large sheets, they can replace fluorescent lights that are currently used in homes and buildings with potentially reduced energy costs for lighting. Full-color capability is an essential feature in organic electroluminescent (OEL) devices for flat panel display. In order to achieve eco-friendly and green technology called solid state lighting, novel designs for red, green, blue and white OEL devices with high performance and good life time are very essential.

11.1. Some of the techniques used for creating white LEDs/OLEDs/displays

- Coat near ultra-violet (NUV) with europium-based red and blue emitting phosphors.
- Selection of suitable proportion of tricolours (RBG), generates white light.
- Coat blue LEDs with quantum dots, which absorb the blue light and emit a warm white light.
- Transfer NUV radiation to visible light through the process of photoluminescence in phosphor materials.

12. Advantages of OLEDs

Different manufacturing process of OLEDs lent itself to many advantages over traditional flat panel displays. OLEDs can be printed onto a substrate using traditional ink jet technology, which can significantly lower the cost than LCDs and plasma displays. A more scalable manufacturing process enables the possibility of much larger displays. OLED screens provide clear and distinct image, even in bright light, they can be viewed from almost any angle up to 160° [184]. OLED displays, produce good brightness and clarity and consistent image quality with good contrast and high luminescence efficiency. Unlike LCDs, they have neither backlights nor chemical shutters that must open or close. Instead each pixel illuminates like a light bulb. OLED pixels turn on and off as fast as any light bulb and hence have fast response time. Thin OLED screens are free from the added bulk and weight of backlighting, making them to differ from compact devices. They are tough enough to use in portable devices such as cell phones, digital video cameras, DVD players, car audio equipment and PDA's. They are as thin as paper, which are lighter and faster, providing full range of colours with high resolution. They can be produced out of plastics, providing the option of flexible OLEDs and displays. They can be operated at low voltages (3–4 V) and at wider temperatures. They are impact resistant and more durable than their glass based counterpart. OLEDs are projected to have full production level cost advantage over most flat panel displays, these remarkable

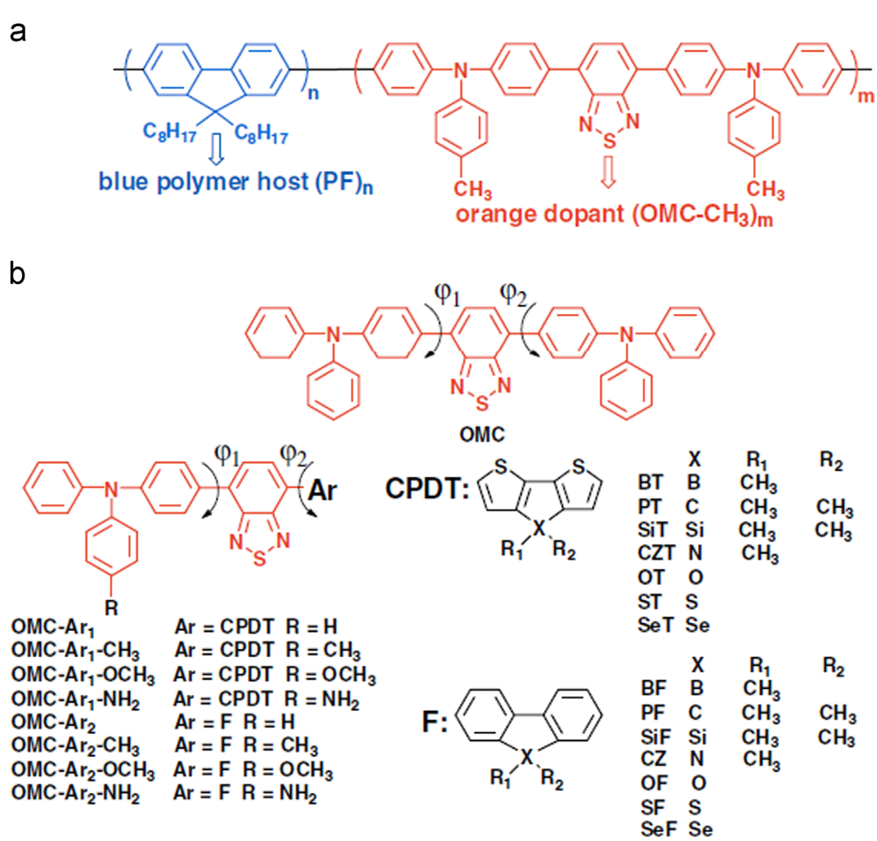


Fig. 14. (a) Chemical structure of model polymer (PF)n-(OMC-CH$_3$)m- (b) investigated BTD based derivatives (OMC and its derivatives) [182].

characteristics can be attributed to the advances in several key areas; new materials, doped guest-host emitters, multilayer device structures, low impedance contacts and a better understanding of the EL process.

13. OLED research hurdles and challenges

Despite of many advantages in OLEDs there are many hurdles to overcome though lot of research is going on to improve OLED's in all aspects. Degradation in OLED has been attributed to various mechanisms including crystallization of organic solids [185,186], electro chemical reactions at the electrode/organic interface [187], migration of ionic species [188] and electro chemical reactions [189]. Cathode oxidation and cathode delamination were shown to be largely responsible for the growth of non emissive spots on the emitting device [190,191].

Some recovery phenomena related to degradation mechanisms in OLEDs were reported by Hadama et al. [192]. It was found that the recoverable degradation could be spontaneously happen or with the assistance of reverse bias [193]. The biggest technical problem left to overcome is the limited lifetime of the organic materials as they are very sensitive to oxygen and moisture. Stability of OLED devices can be improved by protecting them from atmosphere as it plays a major role on device performance. Deposition condition on film morphology may also affect the device performance. Particularly, blue OLEDs typically have lifetimes of around 5000 h when used for flat panel displays, which is lower than typical lifetimes of LCD or Plasma technology. However, recent experimentation has shown that it's possible to swap the chemical component for a phosphorescent one, if the subtle differences in energy transitions are accounted for, resulting in lifetimes of up to 20,000 h for blue PHOLEDs. Deposition conditions also affect the film morphology, affecting device performance. Remarkably, stable devices have been demonstrated in inert environment [194] their life time is severely limited in the presence of humidity and oxygen [195,196]. The lifetime, defined as the time required for the emission to be reduced by half its initial value, of the encapsulated devices is more than 5000 h at 25 °C and 1000 h at 40 °C. These low values of lifetimes are due to fact that no encapsulation is perfectly hermetic and the atmospheric environment has a major impact on the device performance. Intrusion of water into displays damages and destroys the organics, hence improved sealing processes are important for practical manufacturing. Certain technical barriers such as manufacturing cost, life time, driving voltage are still challenging in order to globalize these power saving and eco friendly OLEDs for solid state lighting.

14. OLEDs research trends in past, present and future

The need of sharing and exchanging voluminous data, audio, and video content on round-the-clock basis has been increased in many folds, where in all kinds of communication and computing devices including line-based phones, mobile cellular phones, portable and desktop computers, and personal digital assistants (PDAs), where OLEDs play significant role as a display device. Until 2005, OLEDs were used primarily for testing and by 2005, this technology integrated for many applications and electronic devices and on the long run they are expected to replace LCD displays. White OLEDs are under worldwide investigation as source for general illumination. OLEDs are widely used as light sources, wall decorators, OLED drivers, luminous cloth digital cameras, flat panel displays, flexible displays, computer displays, mobile phones, televisions etc. Especially, SM OLEDs are stealing the march over LCD for being slimmer and more lightweight and power efficient. Current research activities are focused on improving the manufacturing process of OLEDs to make them as cost effective as LCDs. These obvious advantages are working to help OLEDs replace LCDs in the small-sized display segment. A lot of research is being carried out on solid state lighting, which is going to replace the present lighting system. Greater operational lifetime of 10,000 h gives SM OLEDs a slight edge over light-emitting polymers in the general lighting technology, where most applications need lifetimes of more than 20,000 h.

OLED advantages lie ahead on the horizon. Researchers must still struggle with a number of technical challenges including low durability and good life time of OLEDs. Inspite of many improvements in the device performance, unless and until these issues there will be limitations on practical use of OLEDs, and a number of display manufacturers are racing to resolve them in order to expand the possible uses of OLEDs in many applications. With this wide spread of technology there are ideas for heads-up displays, cars displays, billboard-type displays, flat panel TVs, and even flexible displays. High price of coating material also makes high material utilization a priority. There is a lot of research to be done to develop an economical and reliable mass production process and determine new materials. The ideas are endless and almost anything is possible with the new advancements in OLED materials and fabrication technologies.

15. OLEDs: future perspectives

Artificial light extends the day. This light has long been a significant factor contributing to the quality and productivity of human life. As a consequence, large amount of energy is consumed for produce it. Artificial lighting consumes an estimated 0.72% of world gross domestic product, which is large with increasing concern over world energy consumption and hence guidelines and regulations aimed at economizing on consumption of light and associated energy is a big challenge for all researchers at global level. Solid state lighting-the new emerging technology promises better life time, low driving voltage, better efficiencies well beyond those of traditional artificial lighting, accompanied by potentially massive shifts in the consumption of light, the human productivity and energy used associated with that consumption.

Stability of OLED has always been a primary subject for basic research and applications. Substantial worldwide research activities, particularly in Japan on small molecule based OLEDs were triggered by the discovery of Tang and Vanslyke. In 1990, Burroughs and his co-workers at the University of Cambridge, England reported on the first OLED made of a conjugated polymer as the emitting material, which spurred further interest on investigations of organic EL devices [197]. Variety of OLED proto types has been demonstrated and several production facilities are under construction [198]. This growing interest is based on the fact that OLEDs full fill all the essential criteria for a flat panel displays. Many research groups around the world are investigating various organic LEDs, flexible polymer OLEDs and devices based on dendrimers and how to incorporate these devices into display by easy and cheap fabrication techniques. With the introduction of graphene as the device substrate, ITO is going to be replaced by graphene. Currently more than 80 companies, nearly 70 universities and other non-industrial laboratories worldwide are engaged in the field of OLEDs. Once we succeed in finding out the solutions for the hurdles, we can use these OLEDs for SSL, our future lighting will be colourful, prosperous and ecofriendly with these organic displays as light sources, wall decorators, flat panel displays, flexible displays, computer displays, mobile phones, televisions etc.

16. Relevance and influence of OLEDs in the wide lighting sector

Lighting technology is going through a period of technological change with semiconductor based technologies such as organic and inorganic light emitting diodes with new designs, emitting light just at very few volts, leading to the solutions for a wide range of customer requirements. The field of OLEDs is wide open and looks very promising for eco-friendly solid state lighting in the next 3–5 years. This energy-efficient lighting technology plays an important role in reducing global consumption of electricity by almost 50%. The vision of solid state lighting has largely been driven by the desire to reduce energy consumption and pollution free light generation.

17. Conclusions

Review of literature on OLEDs and its materials reveals that the present lighting system consumes around 33% of electricity only for lighting. Significant efforts have been made at global level in order to develop energy efficient and energy saving ecofriendly lighting sources so that we can at least overcome the scarcity of electricity at least to certain extent. Even, global haphazards of currently used lighting systems such as Incandescent lamps, compact fluorescent lamps can be overcome by replacing the present lighting system by green technology called solid state lighting, which is possible only with OLEDs and PLEDs. Researchers should now concentrate on the challenges to improve various factors such as electricity to light conversion efficiency, device stability and life time, material selection, proper encapsulation, methods to maintain uniformity over large areas, novel fabrication technologies, manufacture cost in order to advance this technology and overcome the technical barriers to compete with the present lighting system with the eco-friendly OLEDs. Review of literature on red, blue, green (RBG) and white light emitting materials a range of device architectures reveals various measures to be taken in order to enhance the efficiency and the life time of OLEDs and handling the degradation issues of the organic materials for OLEDs. With these measures if we succeed in improving the efficiency, performance and life time, the present lighting system can be replaced by eco-friendly, energy efficient green technology called solid state lighting, which would play a significant role in reducing global energy consumption.

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